

Supporting Information

Simple ruthenium-catalyzed reductive amination enables the synthesis of a broad range of primary amines

Senthamarai, et al

Supplementary methods

Detailed procedure the preparation of primary amines by Leuckart-Wallach reaction

To a 250ml four-necked flask, equipped with a dropping-funnel, thermometer, water segregator and down-directed condenser, 5 equivalents of ammonium formate were added and stirred at 120°C to melt the solid ammonium formate. After complete melting of ammonium formate, 1-5 mmol of substrate (carbonyl compound) was added and allowed to react for 24 h at 140 °C. Then, the flask was cooled down to the room temperature and the obtained formamide of the corresponding amine was hydrolyzed with 5 equivalents of concentrated aqueous hydrochloric acid (36-38%) by refluxing at 110 °C for 9 h. After cooling to the room temperature, the reaction mixture was diluted with 15 ml of water and filtered. Then the filtrate was extracted with 30ml ether to remove water-insoluble material. The filtrate containing the corresponding amine in HCl salt form was neutralized with aqueous NaOH (15%) and extracted thoroughly with ether (5 x 50 mL). The ether fractions were combined and were evaporated to obtain the corresponding primary amine.

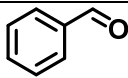
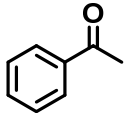
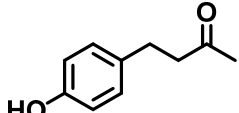
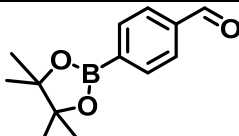
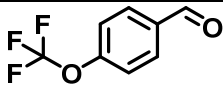
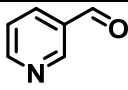
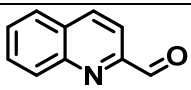
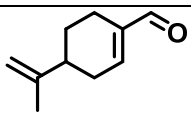
Supplementary note

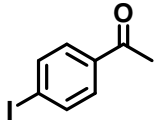
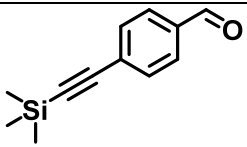
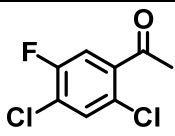
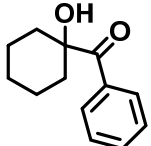
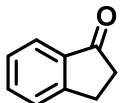
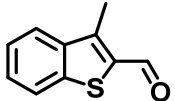
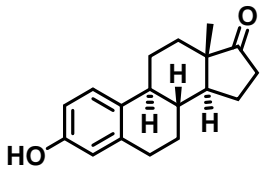
Concentration of **5 in Fig. 1a (manuscript)**

In the concentration-time graph (Fig. 1a), **5** appears to be formed at the beginning of the reaction and then seems to be consumed during further reaction progress. **5**, however, cannot be converted to any other product under our reaction conditions (*vide supra*). We therefore sought for an explanation of the apparent formation and decrease of **5**. As can be seen in Fig. 1d, the hydrogenation activity of the catalyst system drops rapidly for temperatures > 130 °C. Therefore, we expect that while the reaction is cooled down, the hydrogenation reactions quickly ceases, leading to a higher concentration of primary imine. While the thermal energy is still sufficient, the primary imine can then trimerize (which proceeds even at room temperature, see Ref. 78 manuscript) and cyclize (which requires elevated temperature) to form **5**. While this side reaction during cool down would not affect the optimized reaction (since there is no primary imine left after complete hydrogenation), it could occur for incomplete reactions (e.g. when the reaction is stopped prematurely). In line with this reasoning, we found that when the optimized benzaldehyde amination is stopped after just 30 min, 30% yield for **5** is obtained (see Fig. S4). Therefore, we propose that formation and apparent decrease of **5** in the concentration-time profile is an artifact resulting from prematurely quenching the reaction.

Supplementary Tables

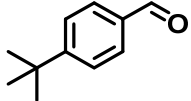
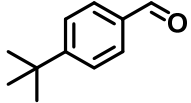
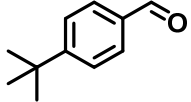
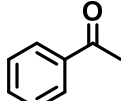
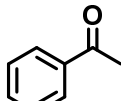
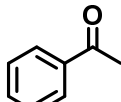
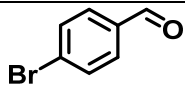
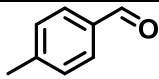
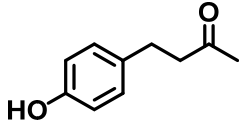
Supplementary Table 1. Preparation of primary amines from aldehydes and ketones by Leuckart-Wallach reaction.

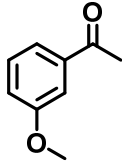
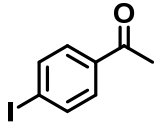
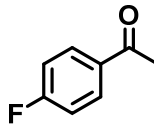
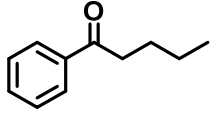
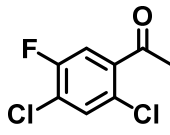
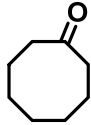
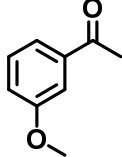
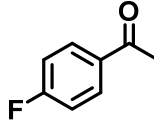
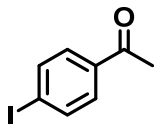
Entry	Aldehyde /Ketone	Conv.	Yield of formamide (GC/GCMS yield)	Yield of primary amine (isolated yield)
1		>99	85% (10% diamino benzyl formamide) (3% tri benzylamine)	75%
2		75%	60% formamide 14% diamine	53% (14% diamine)
3		80%	75%	70%
4		>99%	90% (5-8% of corresponding acid)	5% (84% of benzyl amine. Boronic acid ester group was cleaved)
5		>99%	20% (78% of other products were observed)	15%
6		>99%	25% (20% pyridyl carboxylic acid. 53% other products)	15%
7		>99%	10% (88% quinoline carboxylic acid)	5%
8		>99%	30% (20% one C-C double bond cleaved formamide product. 48% of other products)	10%

9		30%	27%	5% (20% of de-iodo product)
10		>99%	0% (90% N-Benzyl-formamide. 9% benzoic acid. trimethylsilyl group was completely cleaved)	0% (88% benzylamine)
11		<2%	<1%	<1%
12		>99	<2% (95% N-Benzyl-formamide. A cleaved product)	<1% (90% benzylamine)
13		<2%	>1%	-
14		>99%	0% (formamide was not observed. Other products were observed)	0%
15		<1%	<1%	<1%

Reaction conditions: 1-5 mmol of substrate, 5 equivalents of ammonium formate, 140 °C, 24 h. After the formation of corresponding formamide, 5 equivalents of aq. HCl (concentrated 37%) was added and refluxed at 110 °C for 9h and filtered, washed with diethyl ether and then the filtrate was neutralized with NaOH. Finally, the product was extracted thoroughly with ethyl acetate to obtain the corresponding free primary amine.

Supplementary Table 2. Reductive amination of selected aldehydes and ketones using different $\text{RuCl}_2(\text{PPh}_3)_3$ loading

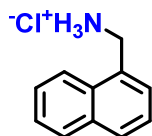
Entry	Aldehyde/ketone	$\text{RuCl}_2(\text{PPh}_3)_3$ loading (mol%)	Conversion	Product (s) (GC yield(s))
1		0.1	80%	0% Primary amine 77% Secondary imine
2		0.5	80%	19% Primary amine 60% Secondary imine
3		1	99%	70% Primary amine 25% Secondary imine 4% Side product 5
4		0.1	10%	9% secondary imine
5		0.5	80%	60% Primary amine 15% Alcohol 20% Secondary imine
6		1	99%	95% Primary amine 5% Alcohol
7		1	99%	99% Secondary imine
8		1	99%	99% Secondary imine
9		1	30%	30% Imine

10		1	30%	25% Primary amine
11		1	30%	20% Primary amine 5% Alcohol
12		1	80%	50% Primary amine 20% Alcohol 10% Secondary imine
13		1	75%	25% Primary amine 50% Alcohol
14		1	40%	20% Primary amine 20% Alcohol
15		1	70	65% Secondary imine
16		2	90%	25% Primary amine 65% Alcohol
17		2	88%	40% Primary amine 48% Alcohol
18		2	85%	70% Primary amine 15% Alcohol

Reaction conditions: 0.5 mmol benzaldehyde/ketone, 0.1-2 mol% $\text{RuCl}_2(\text{PPh}_3)_3$, 5-7 bar NH_3 , 40 bar H_2 1.5 mL t-amyl alcohol, 130 °C, 24 h

NMR data of amines

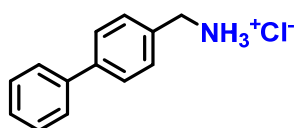
TM5-252



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.64 (br s, 3H), 8.20 – 8.12 (m, 1H), 8.04 – 7.95 (m, 2H), 7.71 – 7.53 (m, 4H), 4.52 (s, 2H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 133.67, 131.12, 130.45, 129.48, 129.10, 127.74, 127.21, 126.69, 125.82, 123.93, 40.81. Brown solid.

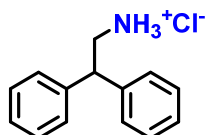
TM5-325



$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.70 (br s, 3H), 7.74 – 7.59 (m, 6H), 7.52 – 7.32 (m, 3H), 4.05 (s, 2H).

$^{13}\text{C NMR}$ (101 MHz, DMSO): δ 140.61, 139.99, 133.76, 130.08, 129.45, 128.13, 127.20, 127.15, 42.24. White solid.

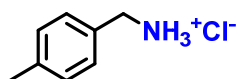
TM5-210



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.24 (br s, 3H), 7.42 – 7.19 (m, 10H), 4.44 (t, $J = 7.8$ Hz, 1H), 3.57 (d, $J = 6.3$ Hz, 2H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 141.53, 129.24, 128.29, 127.47, 48.90, 42.90. Off-White solid.

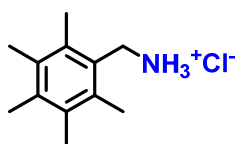
TM5-244



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.62 (br s, 3H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 7.8$ Hz, 2H), 3.94 (s, 2H), 2.29 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 138.08, 131.51, 129.46, 129.46, 42.34, 21.24. White solid.

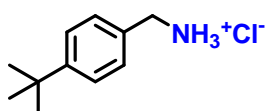
TM5-200



$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.31 (br s, 3H), 4.05 (s, 2H), 2.23 (s, 15H).

$^{13}\text{C NMR}$ (101 MHz, DMSO): δ 135.75, 133.51, 132.70, 128.46, 37.73, 16.97. White solid.

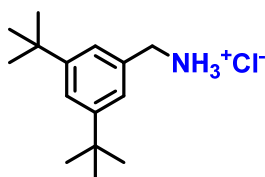
TM5-331



$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.68 (br s, 3H), 7.28 (d, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 3.94 (s, 2H), 1.25 (s, 9H).

$^{13}\text{C NMR}$ (101 MHz, DMSO): δ 151.24, 131.58, 129.29, 125.67, 42.21, 34.76, 31.53. pale Brown solid.

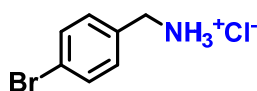
TM5-220



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.61 (br s, 3H), 7.38 (s, 2H), 7.31 (s, 1H), 3.95 (s, 2H), 1.24 (s, 18H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 150.96, 133.50, 123.79, 122.08, 43.16, 35.01, 31.67. White solid.

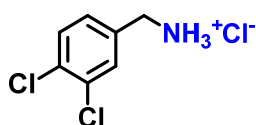
TM5-226



$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.61 (br s, 3H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.51 (d, $J = 8.5$ Hz, 2H), 4.12 (s, 2H).

$^{13}\text{C NMR}$ (101 MHz, DMSO): δ 133.94, 131.85, 131.77, 122.15, 41.90. Brown Solid.

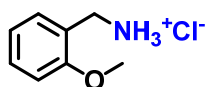
TM5-328



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.72 (br s, 3H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.54 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.04 (s, 2H).

¹³C NMR (75 MHz, DMSO): δ 135.62, 131.70, 131.50, 131.42, 131.07, 130.01, 41.36. White solid.

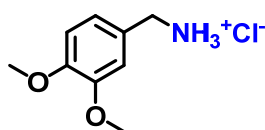
TM5-330



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.52 (br s, 3H), 7.51 – 7.29 (m, 2H), 7.13 – 6.59 (m, 2H), 3.94 (s, 2H), 3.82 (s, 3H).

¹³C NMR (75 MHz, DMSO): δ 157.58, 130.71, 130.56, 122.20, 120.69, 111.34, 56.04, 37.83. Off-White solid.

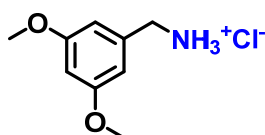
TM5-245



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.63 (br s, 3H), 7.30 (s, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 3.92 (s, 2H), 3.76 (s, 6H).

¹³C NMR (75 MHz, DMSO): δ 149.26, 149.04, 126.79, 121.93, 113.52, 112.00, 56.09, 56.06, 42.50. White solid.

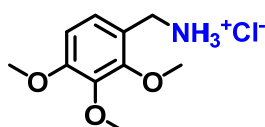
TM5-375



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.83 (br s, 3H), 6.97 (s, 3H), 3.96 (s, 2H), 3.83 (s, 6H).

¹³C NMR (75 MHz, DMSO): δ 160.91, 136.64, 107.36, 100.40, 56.07, 55.80, 42.67. Off-White solid.

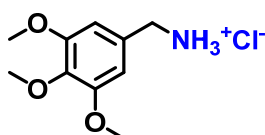
TM5-231



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.56 (br s, 3H), 7.24 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 2H), 3.86 (s, 3H), 3.74 (s, 6H).

¹³C NMR (75 MHz, DMSO): δ 154.32, 151.78, 141.77, 125.21, 119.87, 108.14, 61.51, 60.86, 56.46, 37.13. Off-White solid.

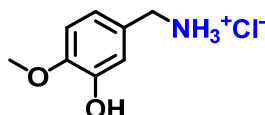
TM5-243



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.71 (br s, 3H), 6.98 (s, 2H), 4.02 (s, 2H), 3.78 (s, 6H), 3.64 (s, 3H).

¹³C NMR (75 MHz, DMSO): δ 153.22, 137.73, 130.06, 107.10, 60.48, 56.52, 42.86. Off-White solid.

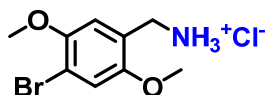
TM5-222



¹H NMR (300 MHz, DMSO-*d*₆): δ 10.12 (br s, 1H), 8.32 (br s, 3H), 7.25 – 6.73 (m, 3H), 3.84 (s, 2H), 3.76 (s, 3H).

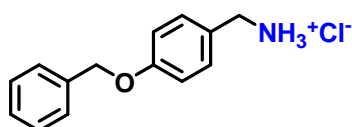
¹³C NMR (75 MHz, DMSO): δ 148.32, 146.87, 126.75, 120.46, 116.78, 112.53, 56.16, 42.40. White solid.

TM5-246



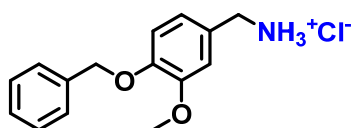
¹H NMR (400 MHz, DMSO-*d*₆): δ 8.63 (br s, 3H), 7.54 (s, 2H), 3.95 (s, 2H), 3.68 (s, 6H).

¹³C NMR (101 MHz, DMSO): δ 151.71, 149.67, 122.51, 116.31, 115.58, 111.18, 57.29, 56.87, 37.33. Off-White solid.

TM5-324

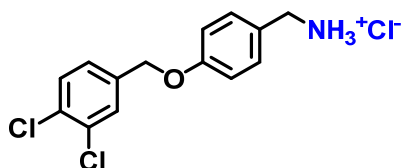
¹H NMR (400 MHz, DMSO-*d*₆): δ 8.53 (br s, 3H), 7.65 – 7.18 (m, 7H), 7.10 – 6.87 (m, 2H), 5.13 (s, 2H), 4.11 (s, 2H).

¹³C NMR (101 MHz, DMSO): δ 158.76, 137.41, 131.04, 128.90, 128.29, 128.08, 126.68, 115.25, 69.61, 42.06. Off-White solid.

TM5-190

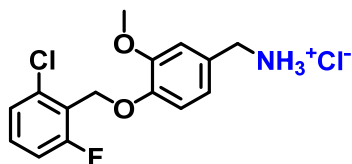
¹H NMR (300 MHz, DMSO-*d*₆): δ 8.50 (br s, 3H), 7.49 – 7.17 (m, 6H), 7.10 – 6.77 (d, *J* = 8.5 Hz, 2H), 5.10 (s, 2H), 3.99 (s, 2H), 3.80 (s, 3H).

¹³C NMR (75 MHz, DMSO): δ 149.48, 148.19, 137.48, 128.88, 128.31, 128.15, 127.12, 121.85, 113.87, 113.73, 70.31, 56.17, 42.56. Off-White solid.

TM5-335

¹H NMR (400 MHz, DMSO-*d*₆): δ 8.55 (br s, 3H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.49 – 7.41 (m, 3H), 7.06 – 7.01 (m, 2H), 5.15 (s, 2H), 3.92 (s, 2H).

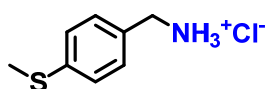
¹³C NMR (101 MHz, DMSO): δ 158.34, 138.70, 131.55, 131.14, 131.10, 130.79, 129.83, 128.20, 127.02, 115.26, 68.03, 40.37. Off-white solid.

TM5-357

¹H NMR (300 MHz, DMSO-*d*₆): δ 8.43 (br s, 3H), 7.51 (td, *J* = 8.2, 6.1 Hz, 1H), 7.41 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.36 – 7.21 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.02 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.12 (s, 2H), 3.95 (s, 2H), 3.74 (s, 3H).

¹³C NMR (75 MHz, DMSO-*d*₆): δ 161.93 (d, *J* = 249.9 Hz), 149.51, 148.11, 135.99 (d, *J* = 5.2 Hz), 132.31 (d, *J* = 10.0 Hz), 127.80, 126.18 (d, *J* = 3.2 Hz), 122.46 (d, *J* = 17.9 Hz), 121.86, 115.22 (d, *J* = 22.4 Hz), 114.12, 113.69, 62.11 (d, *J* = 3.8 Hz), 56.05, 42.52. Off-White solid.

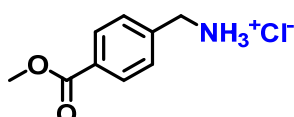
TM5-329



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 8.68 (br s, 3H), 7.50 (d, $J=7.9$ Hz, 2H), 7.31 (d, $J=8.3$ Hz, 2H), 3.94 (s, 2H), 2.46 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, DMSO): δ 138.95, 130.94, 130.18, 126.19, 42.08, 15.11. Brown solid.

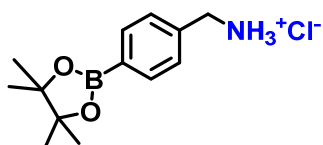
TM5-227



$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 8.75 (br s, 3H), 7.99 (d, $J=8.7$ Hz, 2H), 7.51 (d, $J=8.8$ Hz, 2H), 4.10 (s, 2H), 3.86 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 166.37, 139.91, 129.91, 129.74, 129.69, 52.71, 42.16. Off-White solid.

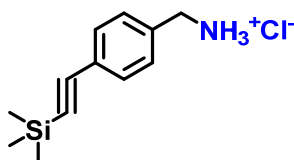
TM5-194



$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 8.61 (br s, 3H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 9.8$ Hz, 2H), 4.02 (s, 2H), 1.29 (s, 12H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 137.82, 134.95, 134.73, 128.79, 84.21, 42.52, 25.13. Off-White solid.

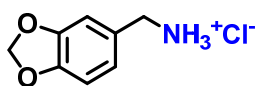
TM5-230



$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 8.23 (br s, 3H), 7.26-7.16 (m, 4H), 3.80 (s, 2H), 0.00 (s, 9H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 134.44, 131.35, 128.83, 121.81, 104.28, 65.98, 41.47, -0.50. Off-White solid.

TM5-336

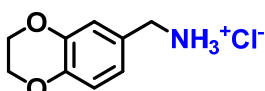


$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.56 (br s, 3H), 7.26 – 6.70 (m, 3H), 6.01 (s, 2H), 3.91 (s, 2H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 147.70, 147.66, 128.00, 123.41, 109.99, 108.65, 101.65, 42.46.

Off-White solid.

M5-183

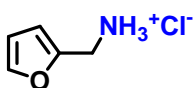


$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.36 (br s, 3H), 7.03 (d, J = 2.0 Hz, 1H), 6.93 (dd, J = 8.3, 2.1 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 4.23 (s, 2H), 3.56 (s, 4H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 143.98, 143.62, 127.30, 122.52, 118.34, 117.53, 64.53, 42.15.

White solid.

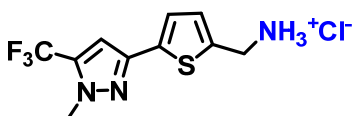
TM5-353



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.74 (br s, 3H), 7.69 (d, J = 1.9 Hz, 1H), 6.70 (d, J = 5.6 Hz, 2H), 4.02 (s, 2H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 147.88, 143.96, 111.38, 110.86, 35.41. Off-White solid.

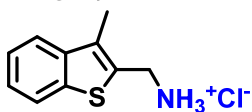
M5-196



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.80 (br s, 3H), 7.45 (d, J = 3.6 Hz, 1H), 7.33 – 7.27 (m, 2H), 4.11 (s, 2H), 3.95 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, DMSO- d_6): δ 145.34, 135.75, 135.55, 132.40 (q, J = 38.8 Hz), 130.27, 125.43, 120.15 (q, J = 268.8 Hz), 105.26, 38.51, 37.25. Pale brown solid.

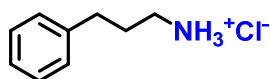
TM5-191



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.73 (br s, 3H), 8.00 – 7.94 (m, 1H), 7.83 – 7.77 (m, 1H), 7.47 – 7.39 (m, 2H), 4.30 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (75 MHz, DMSO): δ 139.97, 139.09, 132.82, 130.16, 125.67, 124.87, 122.99, 122.94, 35.65, 12.10. Pale yellow solid.

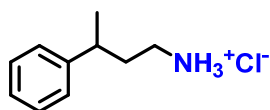
TM5-195



^1H NMR (300 MHz, DMSO- d_6): δ 8.38 (br s, 3H), 7.45 – 6.99 (m, 5H), 2.89 – 2.56 (m, 4H), 1.99 – 1.87 (m, 2H).

^{13}C NMR (75 MHz, DMSO): δ 141.35, 128.82, 128.71, 126.41, 38.79, 32.38, 29.10. Off-White solid.

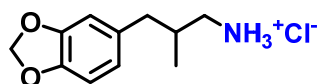
TM5-211



^1H NMR (300 MHz, DMSO- d_6): δ 8.19 (br s, 3H), 7.39 – 7.09 (m, 5H), 2.94-2.78 (m, $J = 7.1$ Hz, 1H), 2.74 – 2.59 (m, 1H), 2.56 – 2.46 (m, 1H), 2.00 – 1.79 (m, 2H), 1.19 (d, $J = 6.9$ Hz, 3H).

^{13}C NMR (75 MHz, DMSO): δ 146.30, 128.94, 127.25, 126.69, 37.79, 36.85, 35.45, 22.49. Off-White solid.

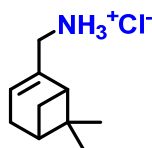
TM5-188



^1H NMR (300 MHz, DMSO- d_6): δ 7.99 (br s, 3H), 6.81- 6.76 (m, 2H), 6.67 (dd, $J = 8.0, 1.6$ Hz, 1H), 5.93 (s, 2H), 3.14 – 1.78 (m, 5H), 0.81 (d, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, DMSO): δ 147.52, 145.80, 133.84, 122.40, 109.74, 108.44, 101.13, 44.30, 33.64, 17.28. Off-White solid.

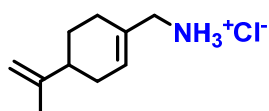
TM5-247



^1H NMR (400 MHz, DMSO- d_6): δ 8.31 (br s, 3H), 5.59 (d, $J = 3.1$ Hz, 1H), 3.34 (s, 2H), 2.56 – 1.91 (m, 6H), 1.25 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (101 MHz, DMSO): δ 141.41, 121.52, 43.66, 43.14, 38.10, 31.41, 31.23, 26.26, 21.30. Brown gum.

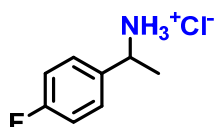
TM5-327



$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.39 (br s, 3H), 5.94 – 5.60 (m, 1H), 4.71 (s, 2H), 3.29 (s, 2H), 2.21 – 2.01 (m, 4H), 1.71 (s, 3H), 1.56 – 1.51 (m, 2H).

$^{13}\text{C NMR}$ (101 MHz, DMSO): δ 149.31, 131.23, 125.94, 109.47, 48.98, 44.07, 30.29, 27.22, 27.01, 21.02. Colorless gum.

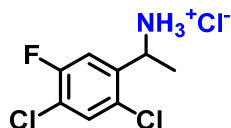
TM5-283



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.66 (br s, 3H), 7.74 – 7.55 (m, 2H), 7.38 – 6.97 (m, 2H), 4.40 (q, J = 6.7 Hz, 1H), 1.53 (d, J = 6.7 Hz, 3H).

$^{13}\text{C NMR}$ (75 MHz, DMSO- d_6): δ 162.34 (d, J = 244.3 Hz), 136.20 (d, J = 3.1 Hz), 129.72 (d, J = 8.3 Hz), 115.82 (d, J = 21.4 Hz), 49.83, 21.24. Pale Brown solid.

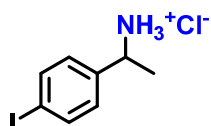
TM5-338



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.88 (br s, 3H), 8.16 (s, 2H), 4.65 (q, J = 6.7 Hz, 1H), 1.51 (d, J = 6.7 Hz, 3H).

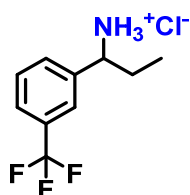
$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 156.81 (d, J = 243.2 Hz), 138.49 (d, J = 6.3 Hz), 131.71 (d, J = 19.4 Hz), 128.00 (d, J = 3.1 Hz), 120.91 (d, J = 18.6 Hz), 116.45 (d, J = 39.4 Hz), 47.29, 20.03. Brown solid.

TM5-337



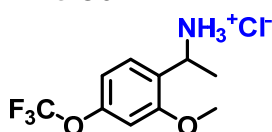
$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.84 – 8.57 (br s, 3H), 7.75 (d, J = 7.9 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 4.34 (q, J = 5.9 Hz, 1H), 1.50 (d, J = 6.7 Hz, 3H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 139.47, 137.80, 129.78, 95.24, 50.09, 21.03. Brown solid.

TM5-356

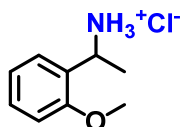
¹H NMR (300 MHz, DMSO-*d*₆): δ 8.83 (br s, 3H), 7.95 (d, *J* = 1.7 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.62 (m, 2H), 4.28 (dd, *J* = 9.2, 5.5 Hz, 1H), 2.30 – 1.61 (m, 2H), 0.73 (d, *J* = 7.4 Hz, 3H).

¹³C NMR (75 MHz, DMSO-*d*₆): δ 139.52, 132.30, 130.19, 129.78 (q, *J* = 31.8 Hz), 125.50 (q, *J* = 2.1 Hz), 124.97 (q, *J* = 3.4 Hz), 124.50 (q, *J* = 272.2 Hz), 55.75, 27.76, 10.29. Brown solid.

TM5-362

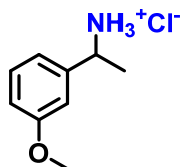
¹H NMR (300 MHz, DMSO-*d*₆): δ 8.74 (br s, 3H), δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.19 – 6.86 (m, 2H), 4.61 – 4.53 (m, 1H), 3.87 (s, 3H), 1.50 (d, *J* = 6.7 Hz, 3H).

¹³C NMR (75 MHz, DMSO): δ 157.73, 149.44, 128.89, 126.94, 122.8 (q, *J* = 255.75 Hz), 112.81, 105.36, 56.75, 44.52, 19.63. Off-White solid.

TM5-265

¹H NMR (300 MHz, DMSO-*d*₆): δ 7.82 (br s, 3H), 7.50 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.35 – 7.25 (m, 1H), 7.04 – 6.91 (m, 2H), 4.53 (q, *J* = 6.7 Hz, 1H), 3.78 (s, 3H), 1.45 (d, *J* = 6.7 Hz, 3H).

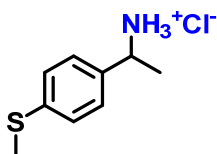
¹³C NMR (75 MHz, DMSO): δ 156.39, 130.08, 127.29, 127.21, 120.99, 111.66, 56.15, 45.04, 19.87. White solid.

TM5-202

¹H NMR (400 MHz, DMSO-*d*₆): δ 8.77 (br s, 3H), 7.31 (s, 1H), 7.31–7.20 (d, *J* = 2.0 Hz, 1H), 7.14 – 7.04 (m, 1H), 6.91 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.33 (q, *J* = 6.7 Hz, 1H), 1.52 (d, *J* = 6.6 Hz, 3H).

¹³C NMR (101 MHz, DMSO): δ 159.85, 141.54, 130.18, 119.36, 114.20, 113.05, 55.72, 50.50, 21.38. White solid.

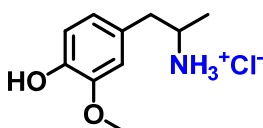
TM5-289



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.61 (br s, 3H), 7.57 (d, *J* = 7.1 Hz, 2H), 7.36 ((d, *J* = 7.9 Hz, 2H)), 4.61 – 4.16 (m, 1H), 2.47 (s, 3H), 1.51 (d, *J* = 6.8 Hz, 3H).

¹³C NMR (75 MHz, DMSO): δ 138.95, 136.23, 127.97, 126.38, 49.01, 21.02, 15.06. Pale brown solid.

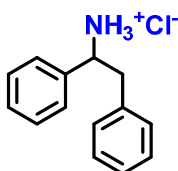
TM5-207



¹H NMR (300 MHz, DMSO-*d*₆): δ 10.05 (br s, 1H), 8.44 (br s, 3H), 6.88 – 6.80 (m, 2H), 6.66 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.03-3.96 (m, 1H), 3.79 (s, 3H), 3.01 (dd, *J* = 13.4, 5.1 Hz, 1H), 2.64 (dd, *J* = 13.3, 8.9 Hz, 1H), 1.18 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (75 MHz, DMSO): δ 147.98, 145.75, 127.90, 121.93, 115.95, 113.75, 56.03, 48.80, 40.63, 17.97. White solid.

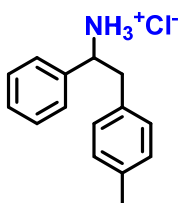
TM5-301



¹H NMR (400 MHz, DMSO-*d*₆): δ 8.11 (br s, 3H), 7.47-7.40 (m, 2H), 7.33 – 7.24 (m, 3H), 7.19 – 6.95 (m, 5H), 4.46 (t, *J* = 7.7 Hz, 1H), 3.57 – 3.41 (m, 1H), 3.13-3.03 (m, 1H).

¹³C NMR (101 MHz, DMSO): δ 137.45, 136.73, 129.67, 128.87, 128.83, 128.69, 128.42, 127.01, 56.44, 42.57. Pale Yellow solid.

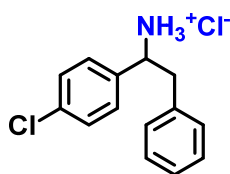
TM5-346



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.10 (br s, 3H), 7.35-7.29 (m, 2H), 7.24-7.19 (m, 2H), 6.97 – 6.78 (m, 5H), 4.36 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.34 (dd, *J* = 13.3, 4.8 Hz, 1H), 3.09 – 2.88 (m, 1H), 2.11 (s, 3H).

¹³C NMR (75 MHz, DMSO): δ 137.21, 135.96, 133.44, 129.47, 129.26, 128.92, 128.85, 128.36, 56.39, 40.46, 21.05. Off-White solid.

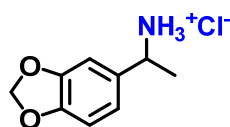
TM5-300



$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 9.02 (br s, 3H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.20 – 7.13 (m, 3H), 7.10 – 6.98 (m, 2H), 4.52 (t, $J = 7.3$ Hz, 1H), 3.64 – 3.31 (m, 2H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 136.54, 136.52, 133.52, 130.44, 129.70, 128.82, 128.77, 127.11, 55.63, 40.50. Pale yellow solid.

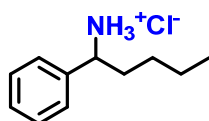
TM5-294



$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 8.56 (br s, 3H), 7.46 (d, $J = 1.7$ Hz, 1H), 7.1 (dd, $J = 8.1, 1.7$ Hz, 1H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.21 (s, 2H), 4.29 (q, $J = 6.1$ Hz, 1H), 1.48 (d, $J = 6.8$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, DMSO): δ 147.82, 147.55, 133.49, 121.12, 108.68, 107.76, 101.65, 50.40, 21.19. Off-White solid.

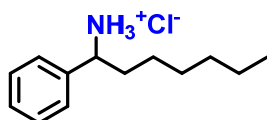
TM5-279



$^1\text{H NMR}$ (300 MHz, $\text{DMSO-}d_6$): δ 8.77 (br s, 3H), 7.64 – 7.50 (m, 2H), 7.39 – 7.29 (m, 3H), 4.35 – 3.93 (m, 1H), 2.24 – 1.63 (m, 2H), 1.40 – 0.89 (m, 4H), 0.78 (t, $J = 7.0$ Hz, 3H).

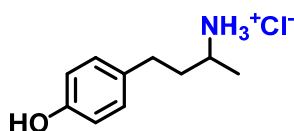
$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 138.53, 129.07, 128.83, 128.03, 55.00, 34.38, 27.67, 22.12, 14.19. Off-White solid.

TM5-413



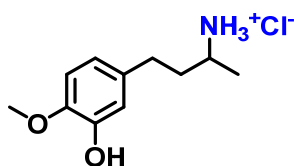
$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ 8.41 (br s, 3H), 7.53 – 7.32 (m, 5H), 4.20–4.14 (t, 1H), 2.01–2.65 (m, 2H), 1.33 – 0.94 (m, 8H), 0.90 – 0.62 (m, 3H).

$^{13}\text{C NMR}$ (101 MHz, DMSO): δ 138.32, 129.22, 129.04, 127.82, 54.91, 34.65, 31.41, 28.54, 25.41, 22.36, 14.34. Off-white solid.

TM5-298

¹H NMR (400 MHz, DMSO-*d*₆): δ 9.30 (br s, 1H), 8.22 (br s, 3H), 7.01(d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 3.08 (dt, *J* = 12.2, 6.1 Hz, 1H), 2.59 – 2.46 (m, 2H), 1.96 – 1.83 (m, 1H), 1.71–1.64 (m, 1H), 1.22 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (101 MHz, DMSO): δ 156.03, 131.30, 129.46, 115.65, 46.86, 36.62, 30.47, 18.46. Off-White solid.

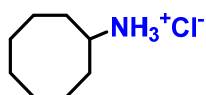
TM5-342

¹H NMR (300 MHz, DMSO-*d*₆): δ 8.82 (br s, 1H), 8.26 (br s, 3H), 7.01 – 6.35 (m, 3H), 3.74 (s, 3H), 3.08 – 2.99 (m, 1H), 2.62 – 2.42 (m, 2H), 2.29 – 1.56 (m, 2H), 1.23 (d, *J* = 6.3 Hz, 3H). **¹³C NMR (75 MHz, DMSO):** δ 147.92, 145.15, 132.12, 120.73, 115.86, 112.99, 56.09, 46.89, 36.49, 30.87, 18.48. Off-White solid.

TM5-274 (Diastereomeric mixture)

¹H NMR (300 MHz, DMSO-*d*₆): δ 8.18 (br s, 3H), 3.21 – 2.76 (m, 1H), 2.08 – 1.82 (m, 2H), 1.74 – 1.65 (m, 1H), 1.56 – 1.23 (m, 4H), 1.03 – 0.83 (m, 2H), 0.78 (s, 9H).

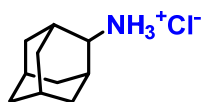
¹³C NMR (75 MHz, DMSO): δ 50.05, 47.47, 46.68, 46.15, 32.71, 32.42, 30.81, 28.86, 27.91, 27.79, 25.38, 20.71. White solid.

TM5-206

¹H NMR (400 MHz, DMSO-*d*₆): δ 8.21 (br s, 3H), 3.23 – 2.97 (m, 1H), 1.91- 1.84 (m, 2H), 1.63- 1.58 (m, 4H), 1.49-1.36 (m, 8H).

¹³C NMR (101 MHz, DMSO): δ 51.36, 30.30, 26.72, 25.30, 23.30. Brown solid.

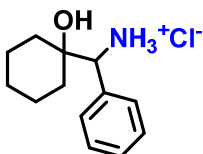
TM5-306



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.40 (br s, 3H), 3.64 – 3.48 (m, 1H), 2.24 – 1.95 (m, 4H), 1.90 – 1.61 (m, 8H), 1.51 (d, J = 13.3 Hz, 2H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 55.18, 37.34, 36.64, 30.38, 29.97, 26.90, 26.82. White solid.

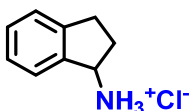
TM5-282



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.35 (br s, 3H), 7.41–7.33 (m, J = 7.2, 2.6 Hz, 2H), 7.40 – 7.32 (m, 3H), 5.03 (s, 1H), 4.11 (s, 1H), 1.85 – 1.65 (m, 1H), 1.64 – 1.40 (m, 4H), 1.38 – 0.97 (m, 5H).

$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 135.84, 129.42, 128.58, 128.33, 71.25, 63.31, 34.85, 32.98, 25.47, 21.47, 21.12. Brown solid.

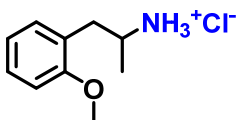
TM5-287



$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 8.50 (br s, 3H), 7.61 (d, J = 7.1 Hz, 1H), 7.31 – 7.29 (m, 3H), 4.70 (dd, J = 8.5, 4.3 Hz, 1H), 3.07 – 2.99 (m, 1H), 2.87 – 2.79 (m, 1H), 2.44 – 2.31 (m, 1H), 2.06 – 1.93 (m, 1H).

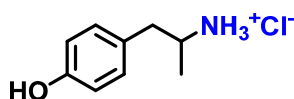
$^{13}\text{C NMR}$ (75 MHz, DMSO): δ 144.39, 139.71, 129.44, 127.11, 125.38, 125.37, 55.12, 30.73, 30.27. Off-White solid.

TM5-415



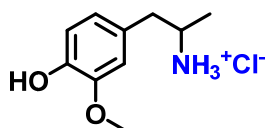
$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.38 – 8.08 (br s, 3H), 7.38 – 7.07 (m, 2H), 7.05 – 6.74 (m, 2H), 3.78 (s, 3H), 3.51 – 3.24 (m, 1H), 3.01 (dd, J = 13.1, 5.1 Hz, 1H), 2.70 (dd, J = 13.1, 9.2 Hz, 1H), 1.09 (d, J = 6.5 Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, DMSO): δ 157.72, 131.36, 128.82, 125.04, 120.84, 111.36, 55.79, 47.15, 35.32, 18.10. White solid.

TM-416

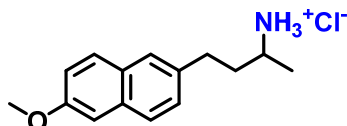
¹H NMR (400 MHz, DMSO-*d*₆): δ 8.27 (br s, 3H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.40 – 3.17 (m, 1H), 3.01 (dd, *J* = 13.4, 4.9 Hz, 1H), 2.75 – 2.59 (m, 1H), 1.16 (d, *J* = 6.4 Hz, 3H).

¹³C NMR (101 MHz, DMSO): δ 156.65, 130.57, 127.18, 115.83, 66.80, 48.79, 17.83. Off-white solid.

TM5-207

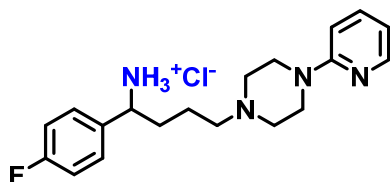
¹H NMR (300 MHz, DMSO-*d*₆): δ 10.05 (br s, 1H), 8.44 (br s, 3H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.66 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.03-3.96 (m, 1H), 3.79 (s, 3H), 3.01 (dd, *J* = 13.4, 5.1 Hz, 1H), 2.64 (dd, *J* = 13.3, 8.9 Hz, 1H), 1.18 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (75 MHz, DMSO): δ 147.98, 145.75, 127.90, 121.93, 115.95, 113.75, 56.03, 48.80, 40.63, 17.97. White solid.

TM-414

¹H NMR (400 MHz, DMSO-*d*₆): δ 8.31 (br s, 3H), 7.81 (m, 3H), 7.45 – 6.96 (m, 3H), 3.82 (s, 3H), 3.30 – 3.00 (m, 1H), 2.93 – 2.63 (m, 2H), 2.18 – 1.63 (m, 2H), 1.28 (d, *J* = 6.5 Hz, 3H).

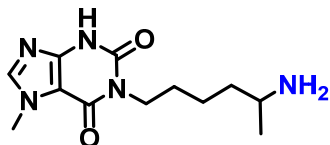
¹³C NMR (101 MHz, DMSO): δ 157.25, 136.54, 133.26, 129.26, 129.01, 128.02, 127.32, 126.40, 118.99, 106.22, 55.59, 47.03, 36.20, 31.28, 18.49. White solid.

TM5-427

¹H NMR (400 MHz, DMSO-*d*₆): δ 8.80 (br s, 3H), 8.14 (d, *J* = 6.6 Hz, 2H), 7.76 (d, *J* = 5.3 Hz, 2H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.32 (t, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 6.6 Hz, 1H), 4.74 – 4.57 (m, 2H), 4.46 – 4.33 (m, 1H), 3.90 – 3.52 (m, 4H), 3.39 – 3.18 (m, 4H), 2.16-2.05 (m, 1H), 1.99-1.87 (m, 1H), 1.82-1.73 (m, 1H), 1.67-1.55 (m, 1H).

¹³C NMR (101 MHz, DMSO): 162.45 (d, *J* = 246.7 Hz), 152.41, 144.56, 138.10, 134.51 (d, *J* = 2.9 Hz), 130.44 (d, *J* = 8.2 Hz), 115.91 (d, *J* = 21.2 Hz), 114.38, 113.24, 54.96, 53.51, 50.12, 43.79, 31.73, 19.90. Pale-yellow solid.

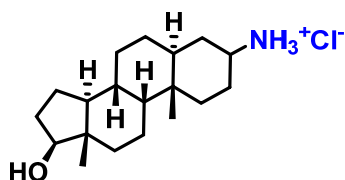
TM5-428



¹H NMR (300 MHz, Methanol-*d*₄): δ 8.07 (s, 1H), 3.92 (s, 3H), 3.91 – 3.85 (m, 2H), 3.22 (d, *J* = 13.4 Hz, 1H), 1.69 – 1.51 (m, 4H), 1.36 (p, *J* = 7.9 Hz, 2H), 1.23 (d, *J* = 6.5 Hz, 3H).

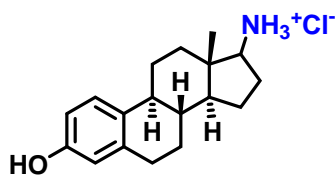
¹³C NMR (75 MHz, MeOD): δ 154.84, 151.28, 146.82, 141.62, 107.36, 40.57, 33.92, 33.22, 29.19, 27.14, 22.31, 17.34. Off-white solid.

TM5-307 (diastereomeric mixture)



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.13 (br s, 3H), 3.48 – 3.15 (m, 2H), 2.09 – 0.99 (m, 22H), 0.89 – 0.66 (m, 3H), 0.67 – 0.35 (m, 3H). **¹³C NMR (75 MHz, DMSO-*d*₆):** δ 80.48, 53.63, 51.17, 46.69, 43.01, 38.40, 37.10, 35.98, 35.49, 31.59, 31.26, 30.97, 30.29, 28.22, 24.28, 23.50, 20.40, 11.79, 11.55. White solid.

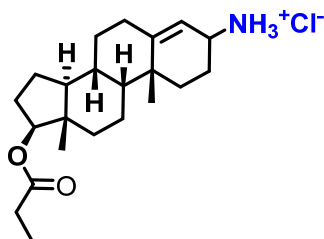
TM5-363 (diastereomeric mixture)



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.14 (br s, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.65 – 6.25 (m, 2H), 3.22–2.71 (m, 3H), 2.45–2.05 (m, 3H), 1.87 – 1.12 (m, 10H), 0.76 (d, *J* = 4.4 Hz, 3H).

¹³C NMR (101 MHz, DMSO): δ 155.58, 155.56, 137.46, 137.44, 130.41, 130.29, 126.57, 126.48, 115.47, 115.46, 113.32, 113.29, 59.98, 59.26, 51.30, 47.95, 43.90, 43.59, 43.29, 42.52, 38.75, 38.70, 36.26, 32.41, 29.67, 29.56, 28.40, 28.28, 27.53, 26.73, 26.21, 26.13, 24.69, 23.57, 18.36, 12.18. White solid.

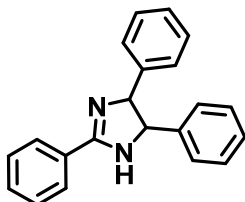
TM5-311 (diastereomeric mixture)



¹H NMR (300 MHz, DMSO-*d*₆): δ 7.52 (br s, 3H), 5.26–5.19 (m, 1H), 4.48 (dd, *J* = 9.1, 7.6 Hz, 1H), 3.62–3.53 (m, 2H), 2.36 – 1.18 (m, 17H), 1.09 – 0.89 (m, 8H), 0.67 (t, *J* = 34.4 Hz, 3H), 0.63–0.59 (m, 1H).

¹³C NMR (75 MHz, DMSO): δ 174.07, 149.61, 117.36, 82.11, 53.97, 50.13, 47.73, 42.59, 37.14, 35.46, 32.37, 31.99, 29.09, 27.50, 24.21, 23.49, 20.58, 18.93, 12.31, 9.61. HRMS (ESI): Calcd for C₂₂H₃₅O₂N₂ [M]⁺ 345.26601; found 345.26632. Off-white solid.

TM5-493



¹H NMR (300 MHz, DMSO-*d*₆): δ 8.13–8.01 (m, 2H), 7.60 – 7.42 (m, 4H), 7.09 – 6.92 (m, 10H), 5.45 (s, 2H).

¹³C NMR (75 MHz, DMSO): δ 164.25, 140.51, 131.08, 130.79, 128.84, 128.02, 127.91, 127.71, 126.69, 70.03. HRMS (ESI): Calcd for C₂₁H₁₈N₂ [M]⁺ 298.14657; found 298.14645. Pale yellow gum.

AAS analysis of purified benzylamine to determine Ru content

Dateiname 18062102

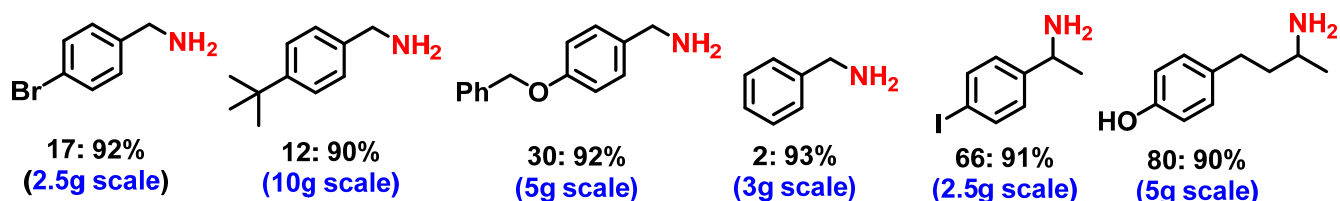
Instrument: contrAA 800D # Tech: Flamme

SW-Version: ASpect CS 2.2.1.0 Created: 21.06.2018 10:32

Datum	Zeit	Name(2)	Linie	Konz.2	Einheit	Ext.
21.06.2018	10:18	Thiru TM 5	Ru349	Messwert 0.000	M- %	0.000
21.06.2018	10:19	Thiru TM 5	Ru349	Ru n.n.	M- %	0.000

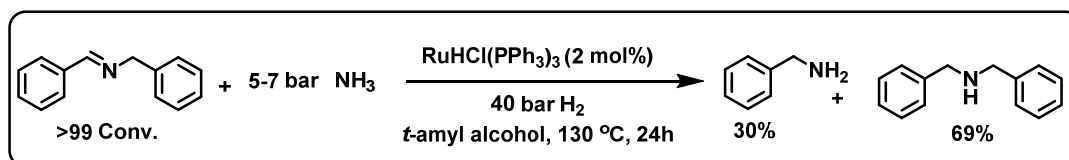
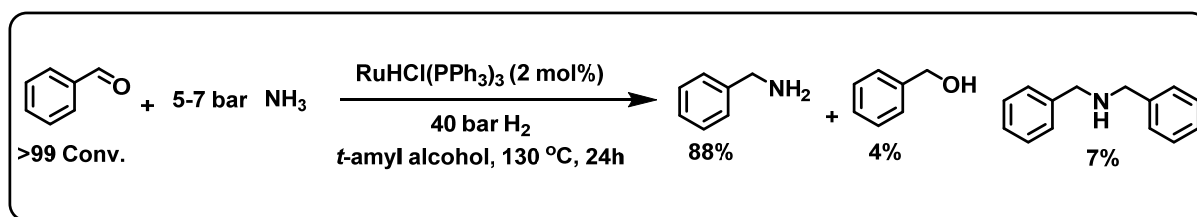
AAS measurement for the detection of metal content in the isolated and purified amine product.

Supplementary Figures

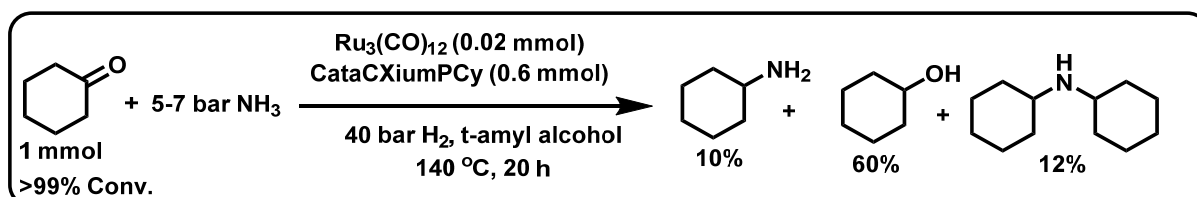
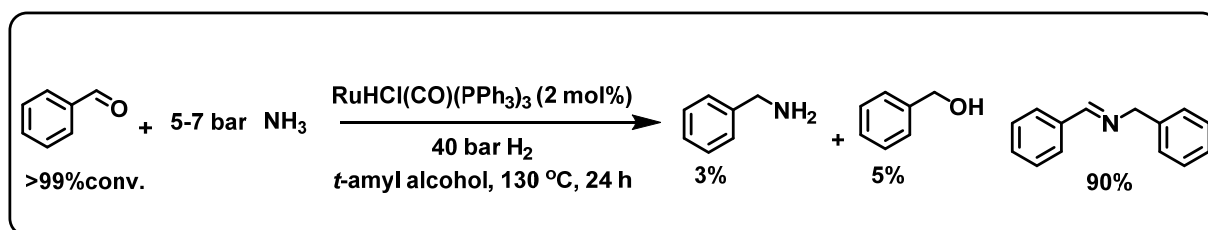


Supplementary Figure 1. Demonstrating the synthetic utility for gram-scale reactions.

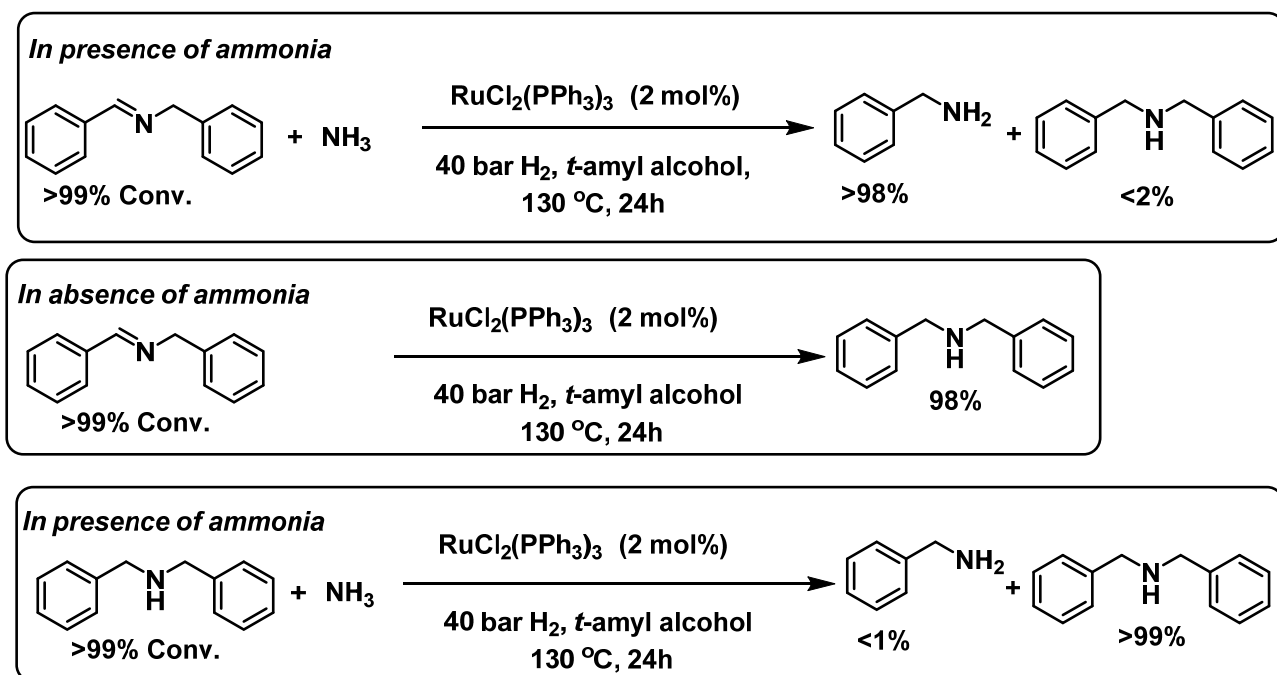
Reaction conditions: 2-20 g carbonyl compound, 2-3 mol% of $\text{RuCl}_2(\text{PPh}_3)_3$ (2 mol% in case of aldehyde, 3 mol% in case of ketone), 5-7 bar NH_3 , 40 bar H_2 , 25-150 mL *t*-amyl alcohol, 130 °C, 24-30 h. Isolated as free amines and converted to hydrochloride salts. Corresponding hydrochloride salts were subjected to NMR analysis.



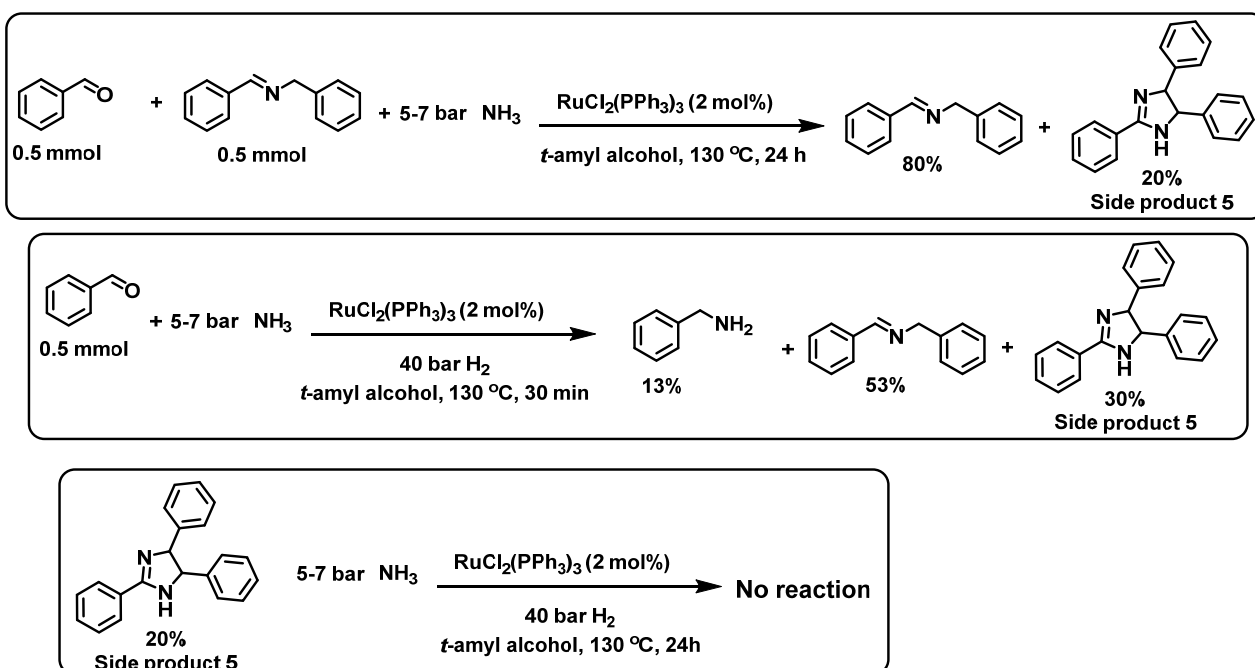
Supplementary Figure 2. Reductive amination of benzaldehyde and N-benzylidenebenzylamine using $\text{RuHCl}(\text{PPh}_3)_3$.



Supplementary Figure 3. Reductive amination of benzaldehyde using $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and cyclohexanone using $\text{Ru}_3(\text{CO})_{12}/\text{CataCxiuPCy}$.

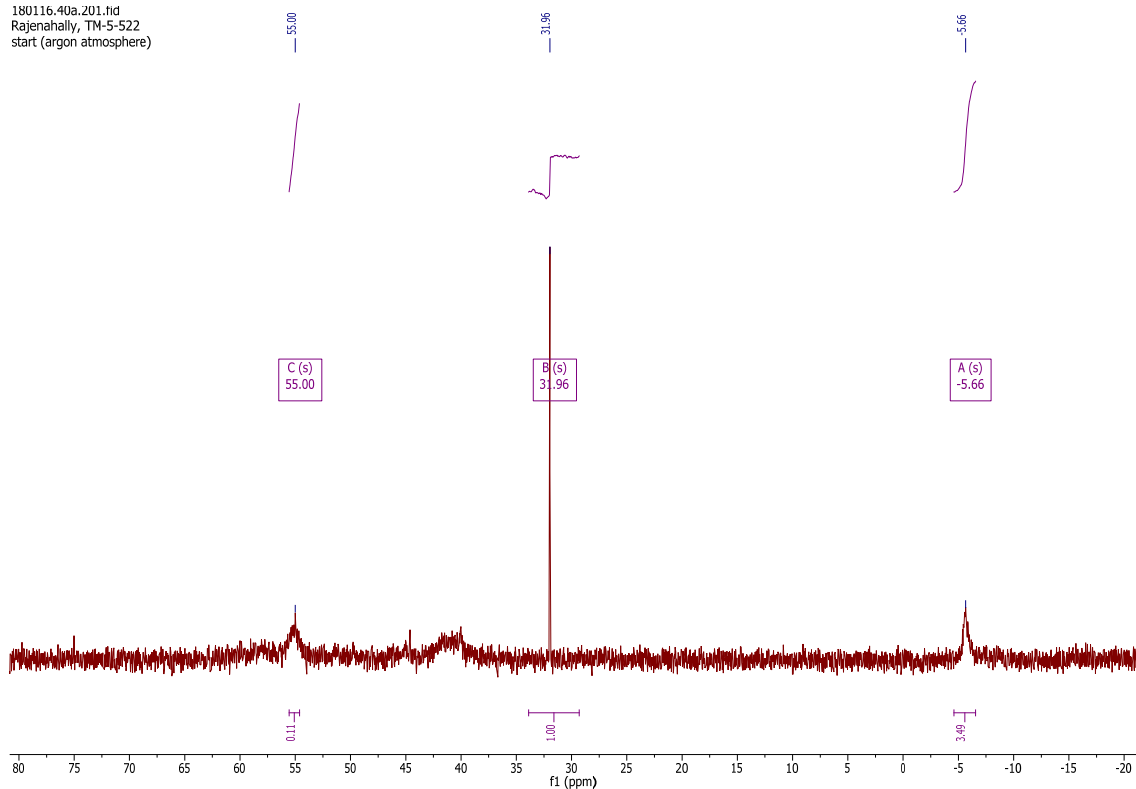


Supplementary Figure 4. Reaction of *N*-benzylidenebenzylamine and dibenzylamine in presence and absence of ammonia with $\text{RuCl}_2(\text{PPh}_3)_3$ and hydrogen.



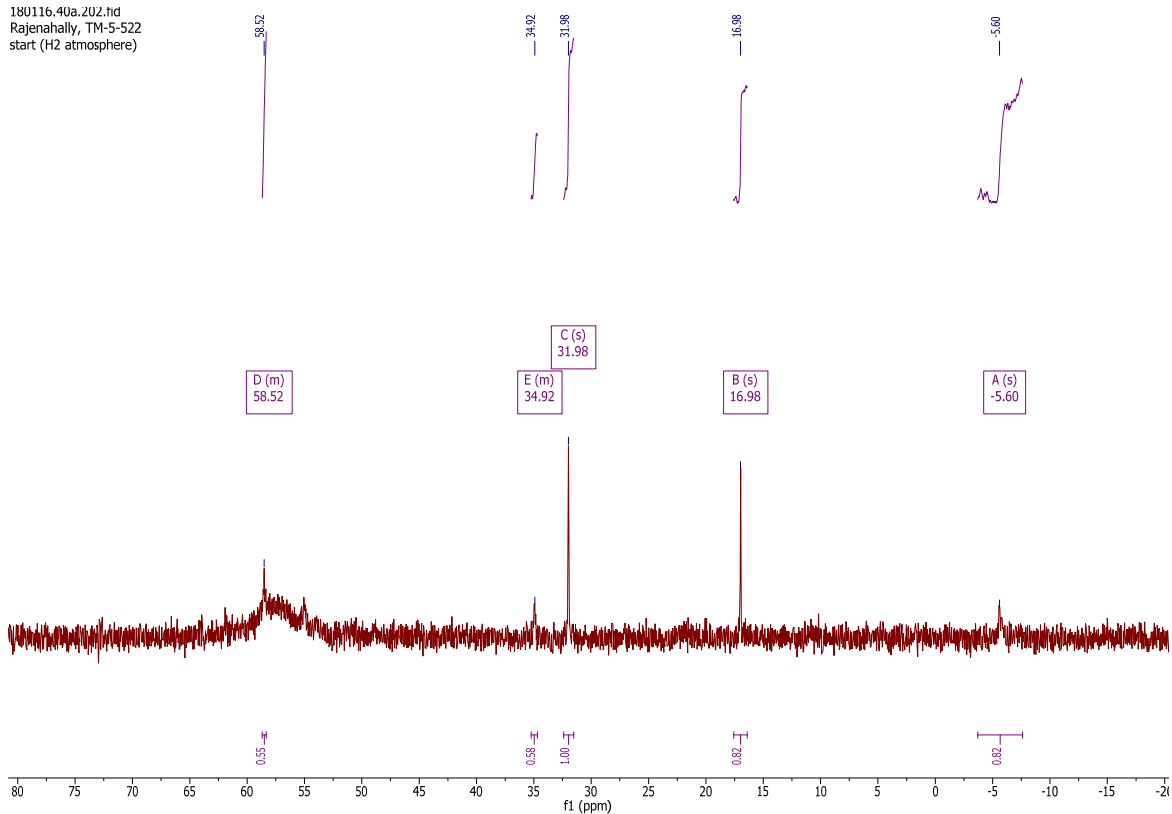
Supplementary Figure 5. Controll reactions to confirm the formation of side product 5.

180116.40a.201.hid
Rajenahally, TM-5-522
start (argon atmosphere)



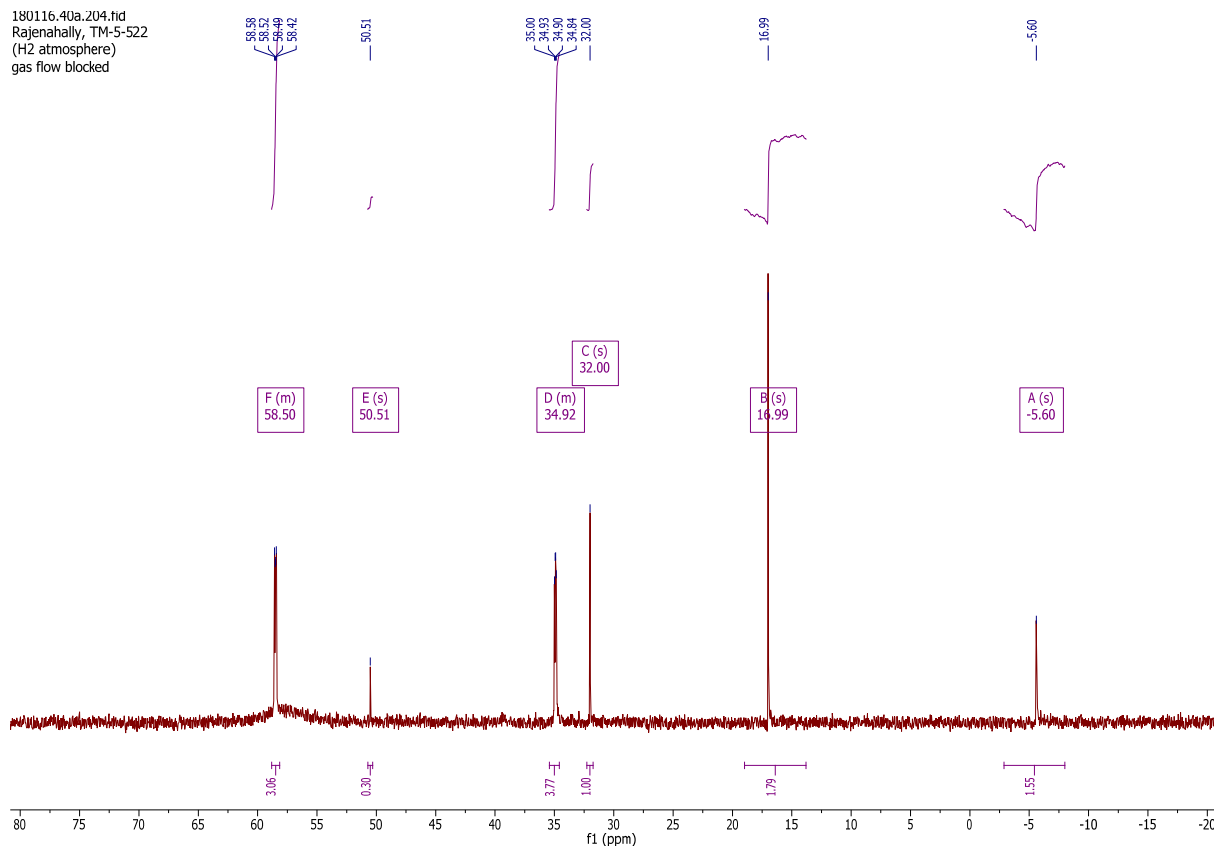
Supplementary Figure 6. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -20 to 80 ppm) of $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, C_6D_6 at RT, argon atmosphere.

180116.40a.202.hid
Rajenahally, TM-5-522
start (H2 atmosphere)



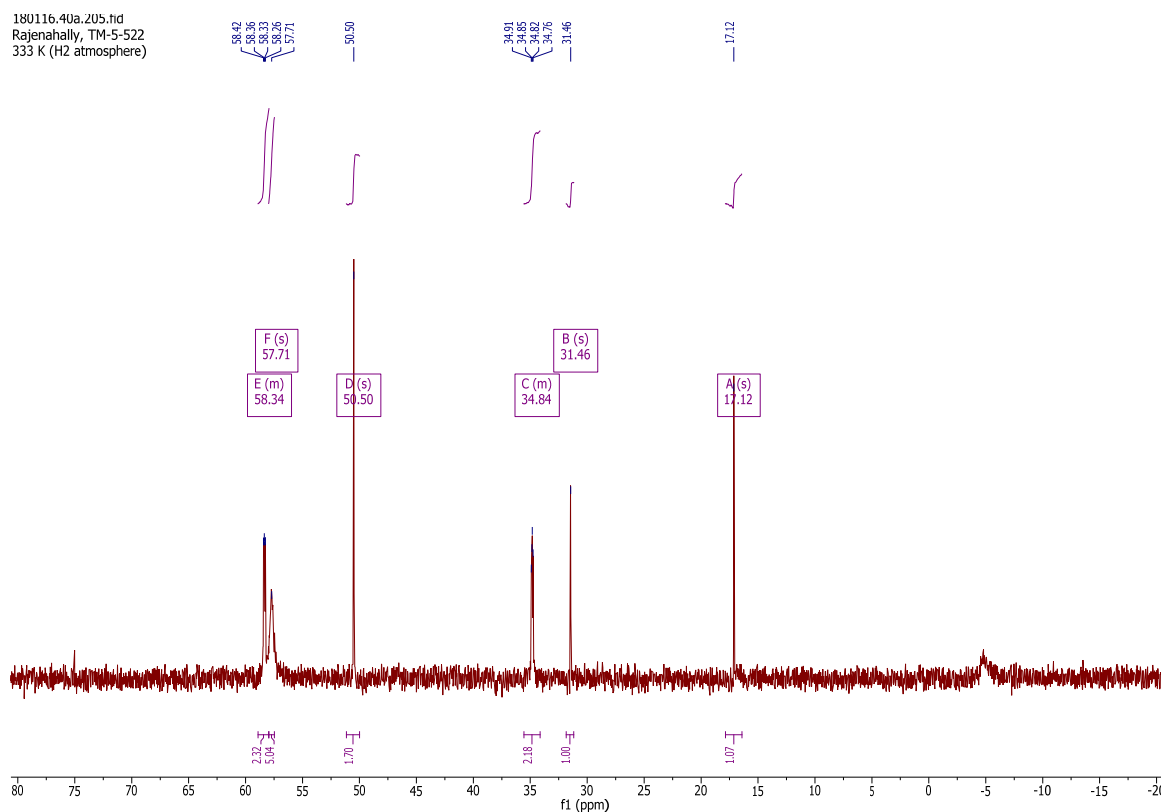
Supplementary Figure 7. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -20 to 80 ppm) of $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, C_6D_6 at RT, H_2 atmosphere (1.5 bar), 10 min.

180116.40a.204.fid
Rajenahally, TM-5-522
(H₂ atmosphere)
gas flow blocked



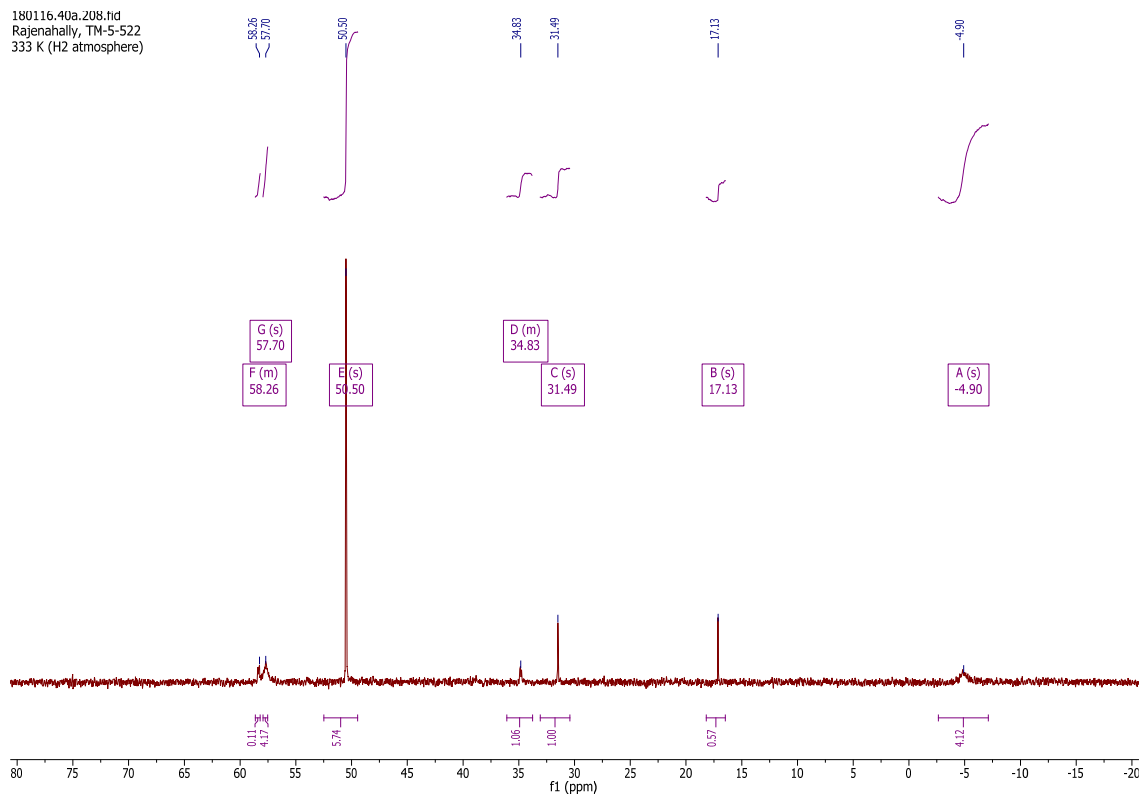
Supplementary Figure 8. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -20 to 80 ppm) of $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, C_6D_6 at RT, H_2 atmosphere (1.5 bar), 2.5h.

180116.40a.205.fid
Rajenahally, TM-5-522
333 K (H₂ atmosphere)



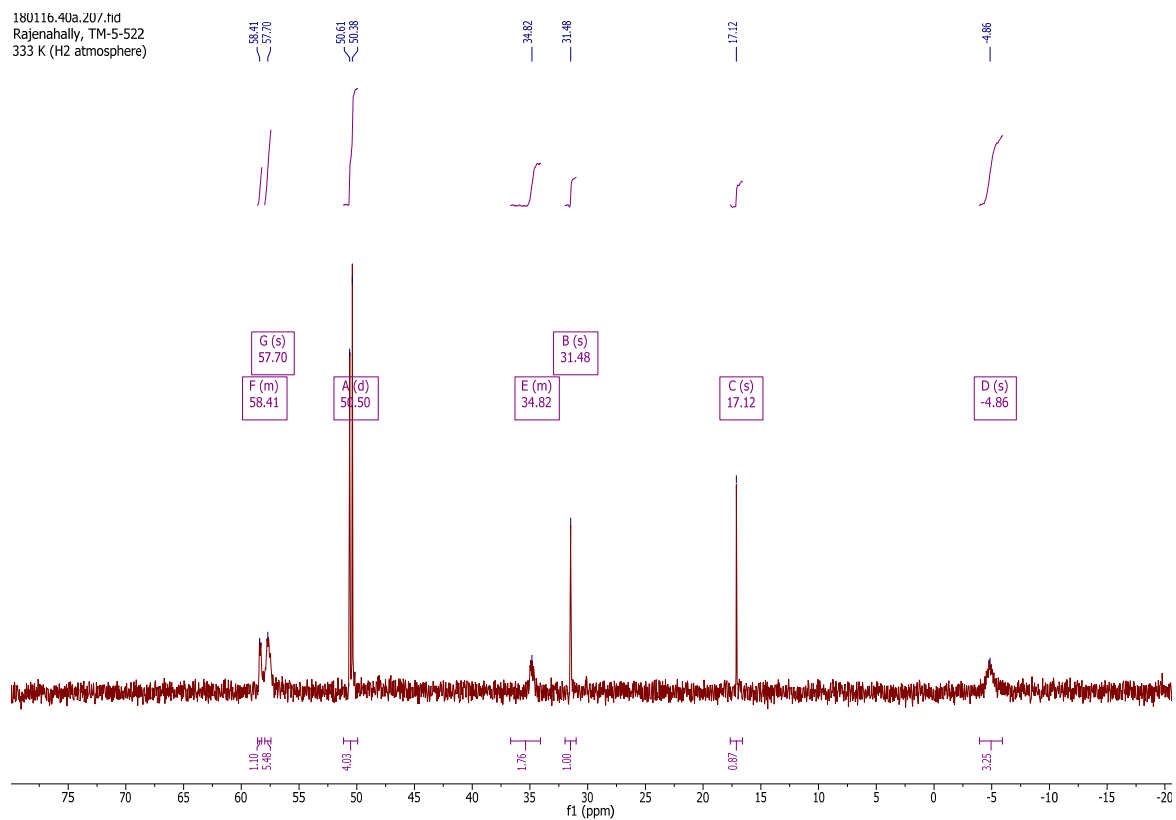
Supplementary Figure 9. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -20 to 80 ppm) of $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, C_6D_6 at 60°C, H_2 atmosphere (1.5 bar), 30 min.

180116.40a.208.hd
Rajenahally, TM-5-522
333 K (H2 atmosphere)

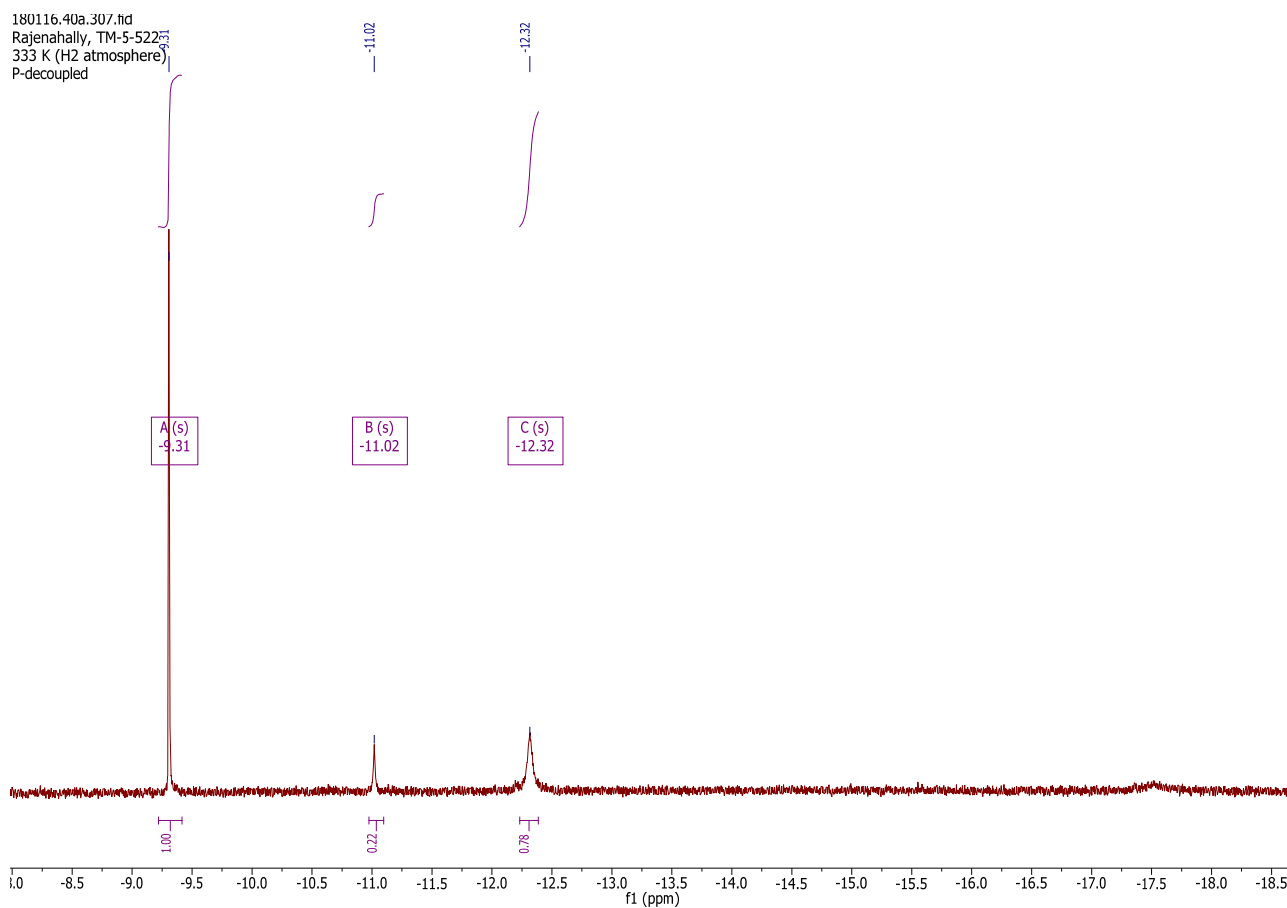


Supplementary Figure 10. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -20 to 80 ppm) of $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, C_6D_6 at 60°C , H_2 atmosphere (1.5 bar), 2.5h.

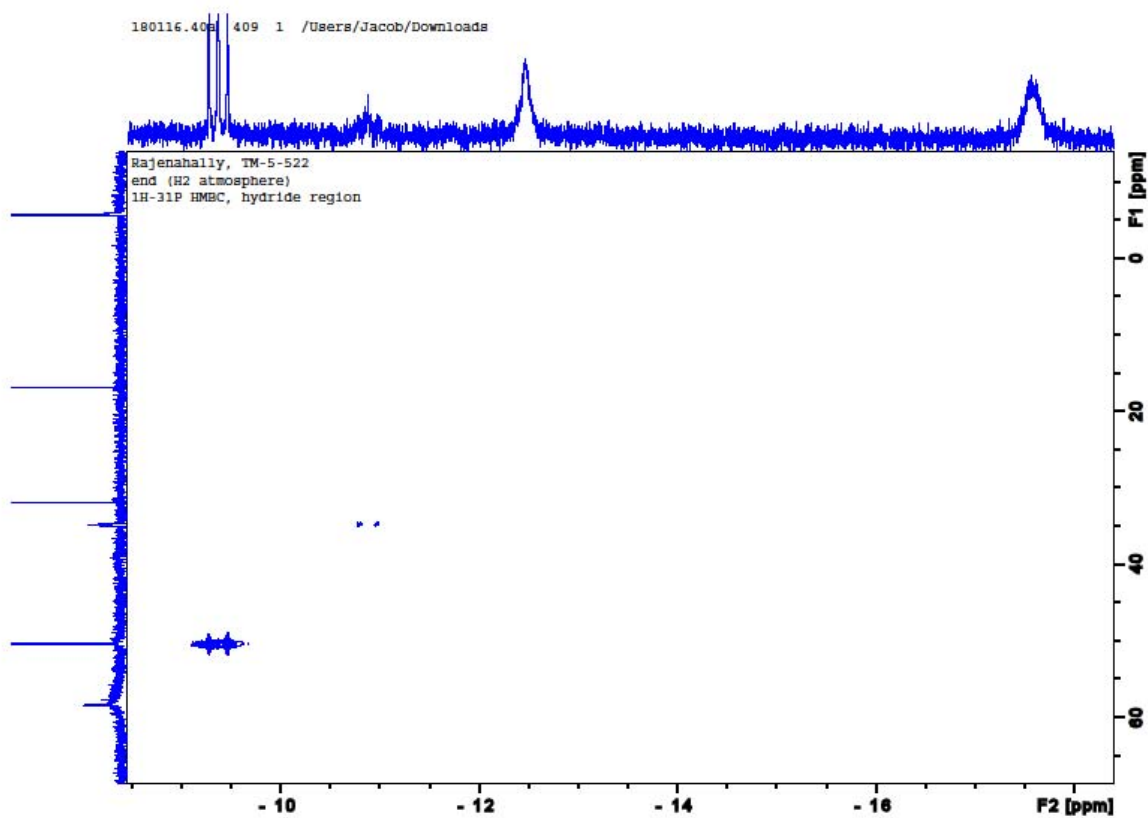
180116.40a.207.hd
Rajenahally, TM-5-522
333 K (H2 atmosphere)



Supplementary Figure 11. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, -20 to 80 ppm) of $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, C_6D_6 at 60°C , H_2 atmosphere (1.5 bar), 1.5h, decoupled with reduced power (only aromatic protons are decoupled).

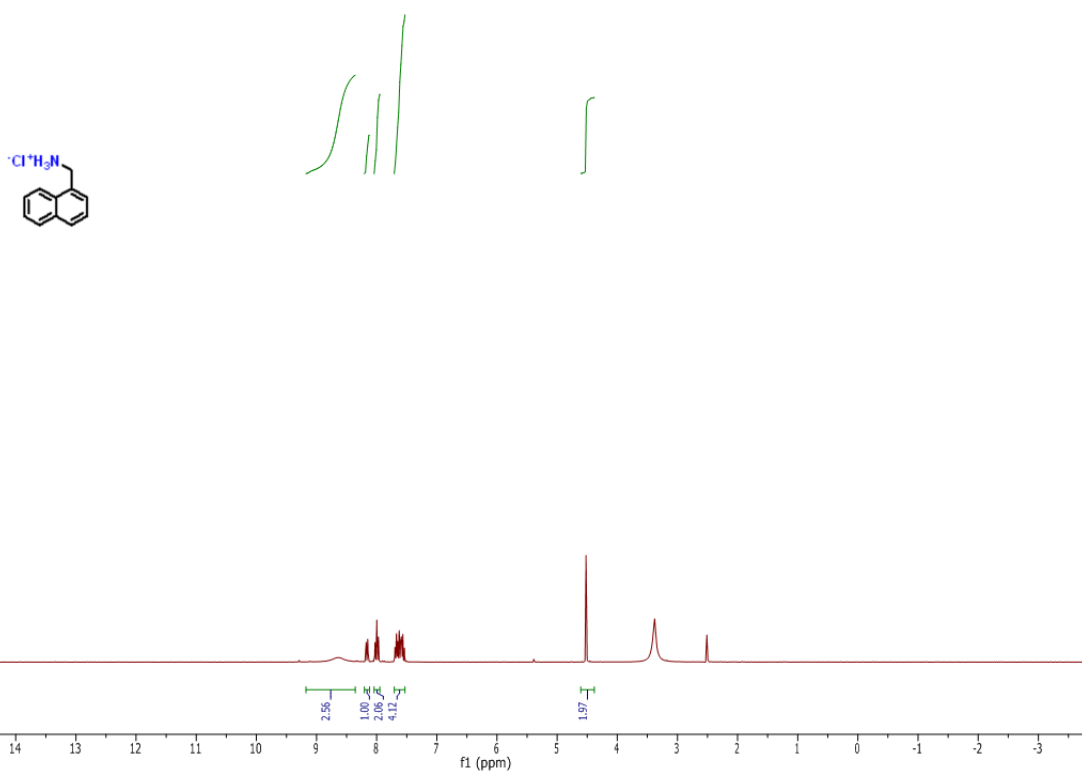


Supplementary Figure 12. $^1\text{H}\{^{31}\text{P}\}$ NMR (400 MHz, -18 to -8 ppm) of $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, C_6D_6 at 60°C , H_2 atmosphere (1.5 bar), 1.5h.



Supplementary Figure 13. ^1H - ^{31}P HMBC NMR (400 MHz for ^1H) of $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, C_6D_6 after 2.5h at 60°C under H_2 atmosphere (1.5 bar), measured at RT under H_2 atmosphere.

171004.f319.10.fid
Thiru TM5-252
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 19

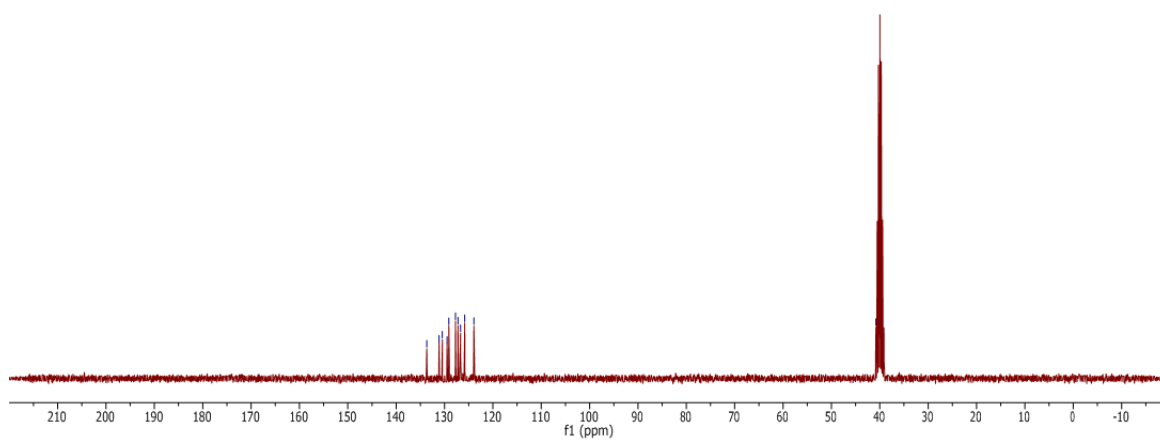


Supplementary Figure 14. ¹H NMR spectrum

171004.f319.11.fid
Thiru TM5-252
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 19

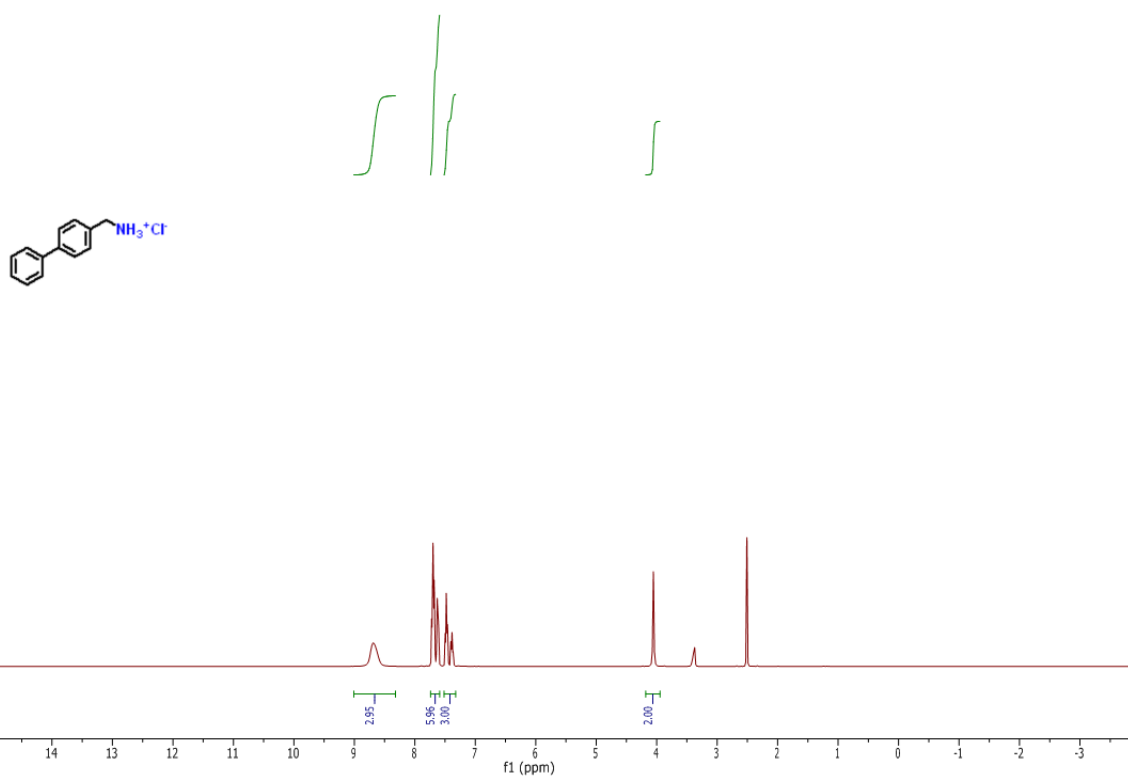
133.67
133.45
130.45
129.88
129.10
127.74
127.21
126.82
126.82
123.93

40.81



Supplementary Figure 15. ¹³C NMR spectrum

1/0914.416.10.nd
Kathir TMS-325
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 16

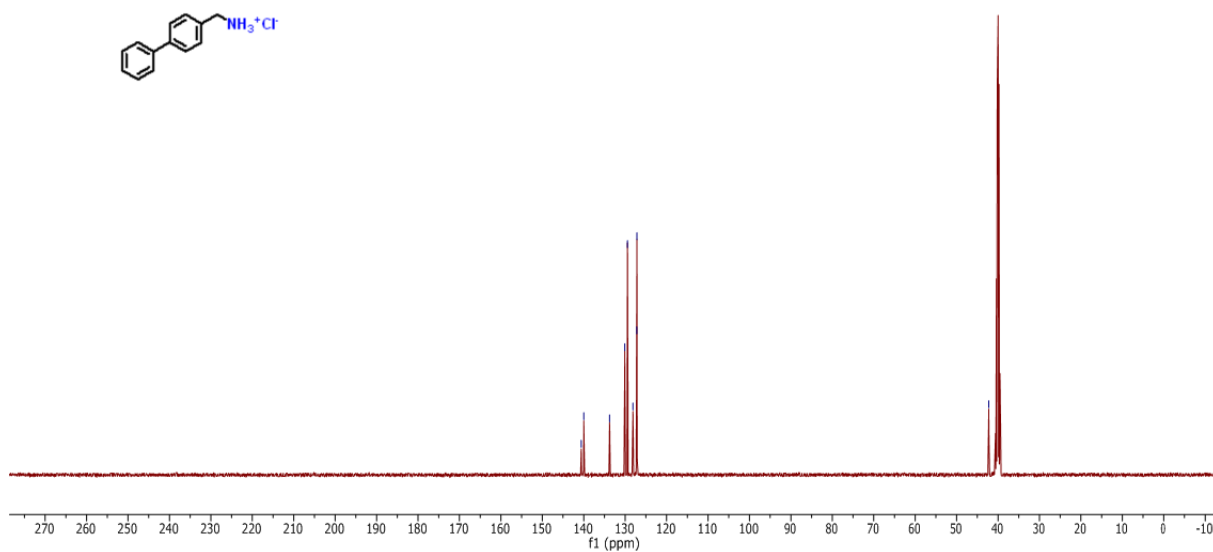


Supplementary Figure 16. ^1H NMR spectrum

1/0914.416.11.nd
Kathir TMS-325
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 16

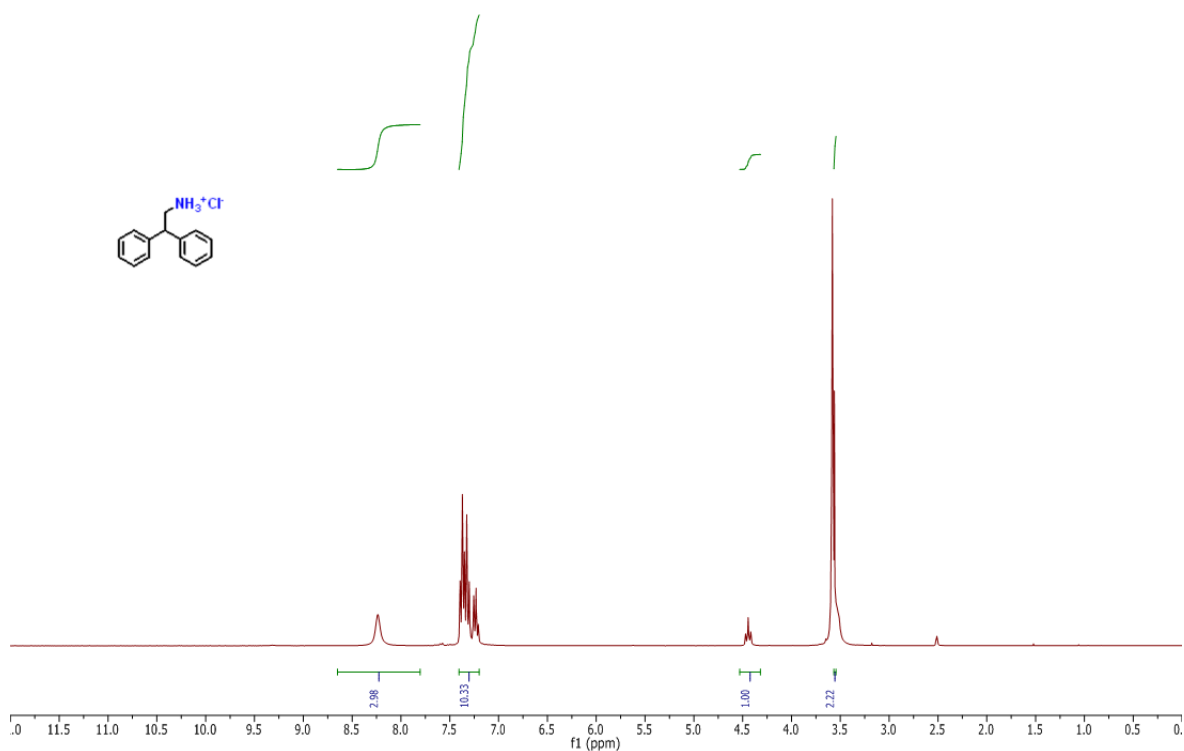
140.61
139.99
133.76
130.08
129.45
128.13
127.20
127.15

42.24



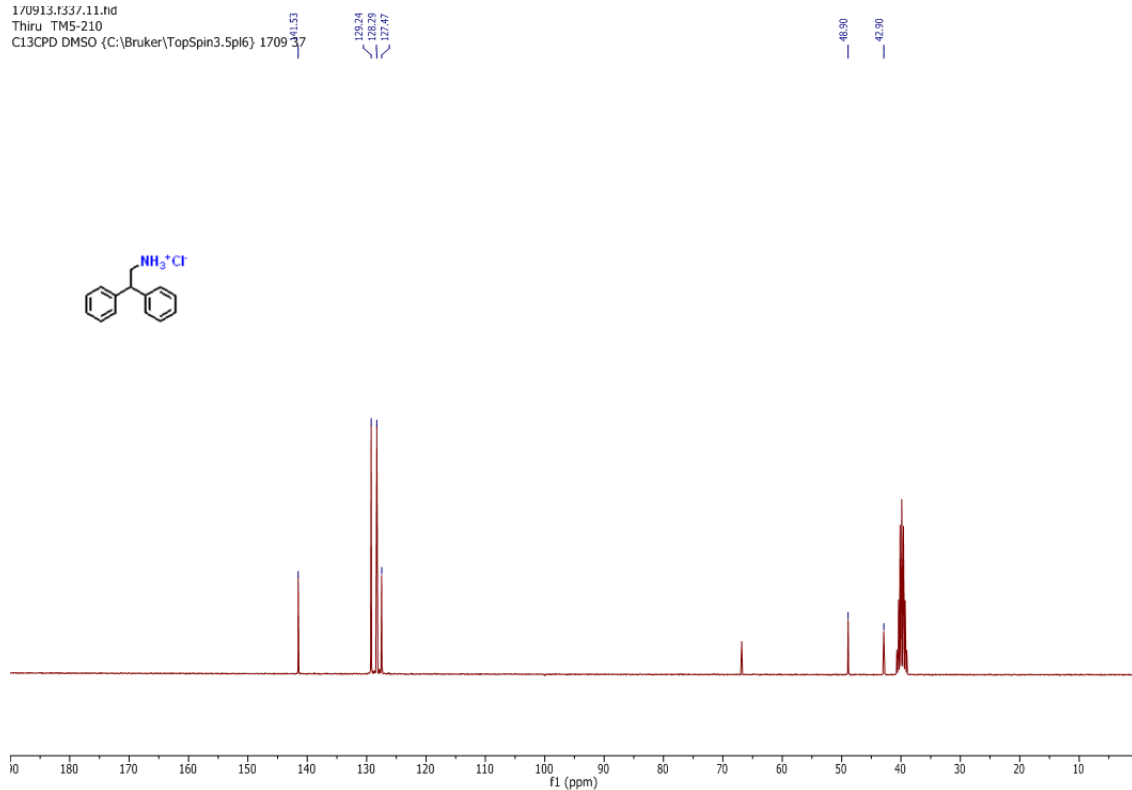
Supplementary Figure 17. ^{13}C NMR spectrum

170913.f337.10.nd
Thiru TM5-210
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 37



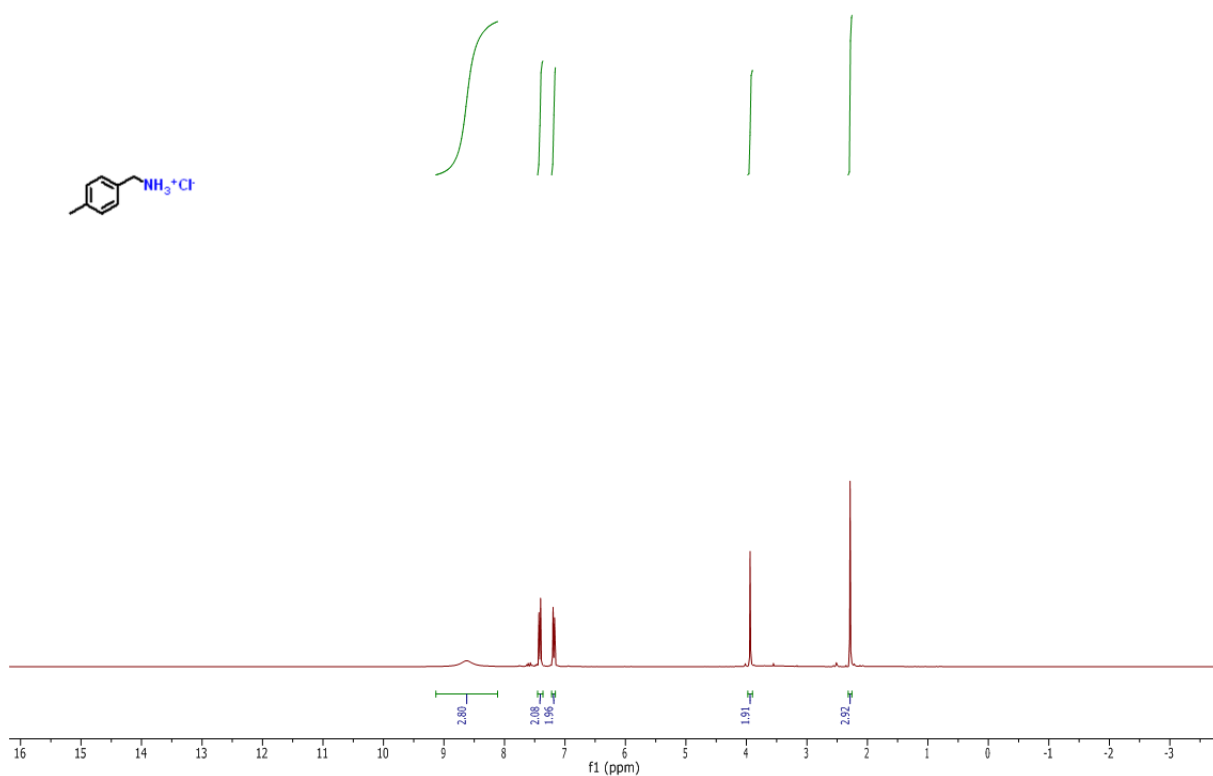
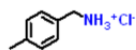
Supplementary Figure 18. ¹H NMR spectrum

170913.f337.11.nd
Thiru TM5-210
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 37



Supplementary Figure 19. ¹³C NMR spectrum

170926.f312.10.fid
Thiru TMS-244
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 12



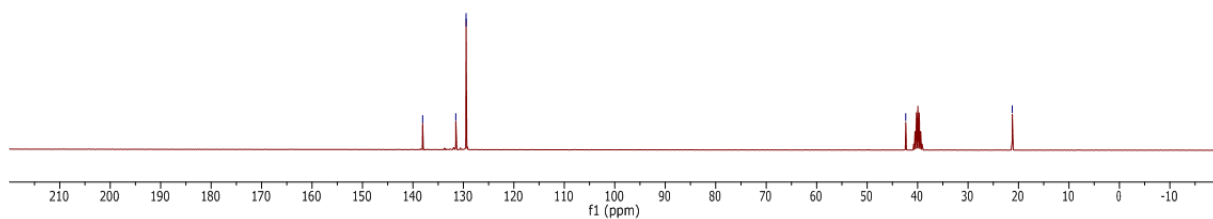
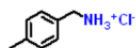
Supplementary Figure 20. ¹H NMR spectrum

170926.f312.11.fid
Thiru TMS-244
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 12

138.08
131.51
129.46
129.46

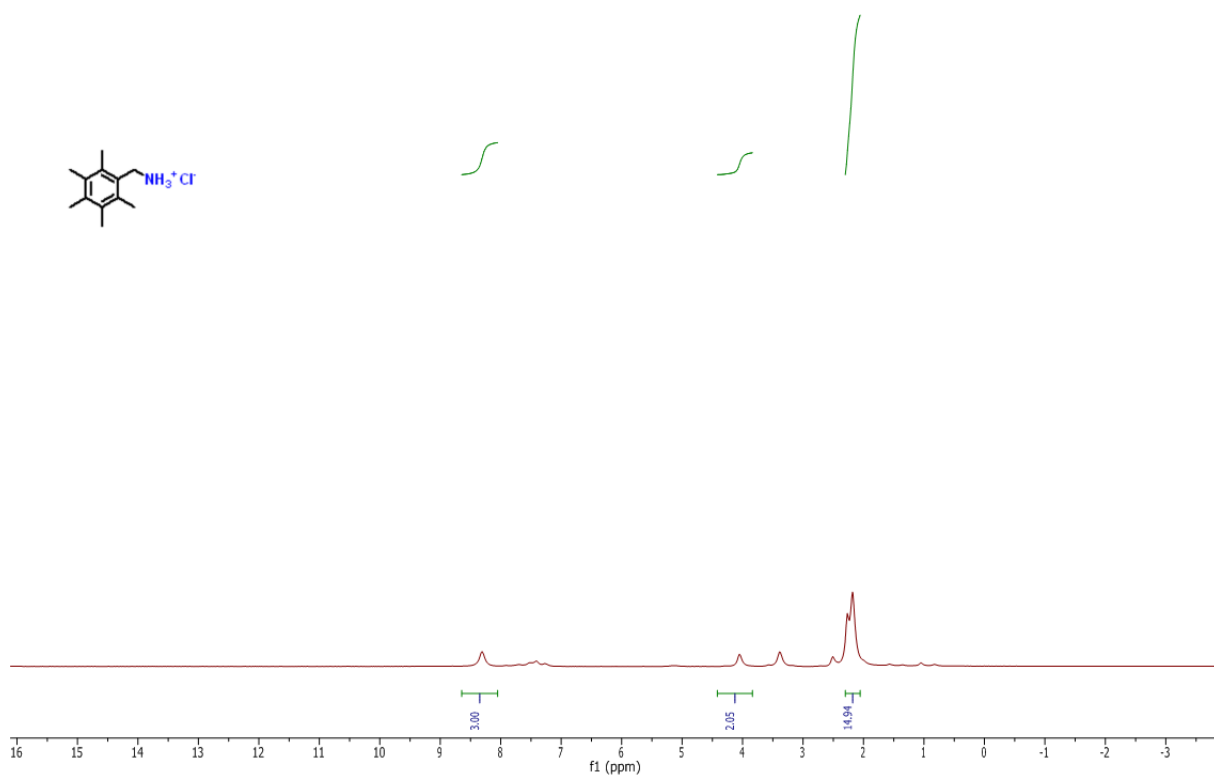
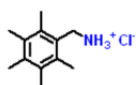
42.34

21.24



Supplementary Figure 21. ¹³C NMR spectrum

1/0926.424.10.nd
Thiru TMS-200
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 24



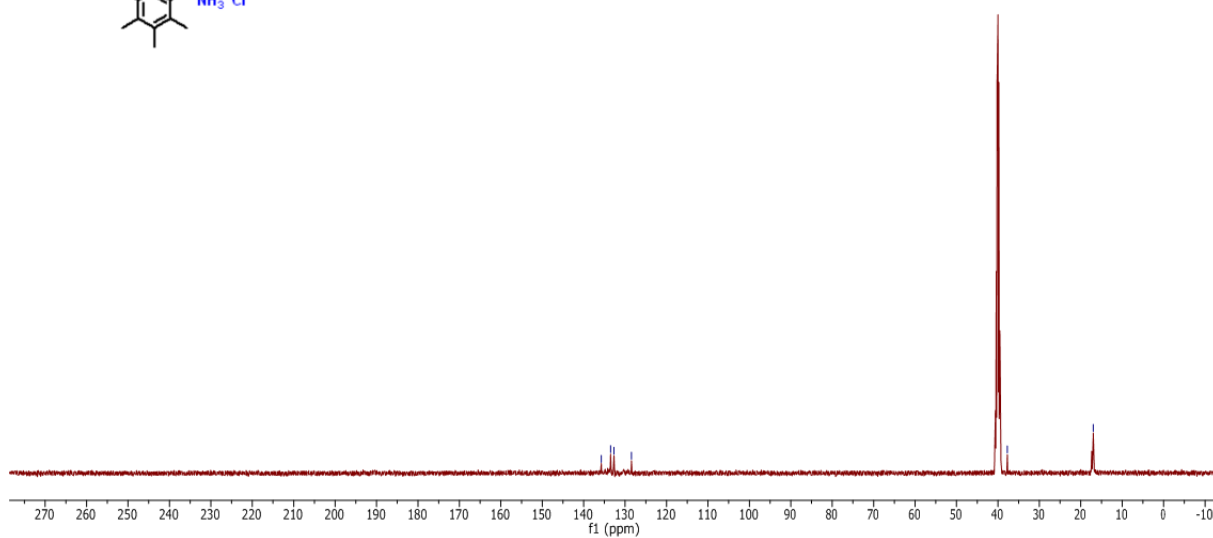
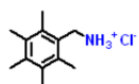
Supplementary Figure 22. ¹H NMR spectrum

1/0926.424.11.nd
Thiru TMS-200
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 24

135.75
133.61
132.70
128.46

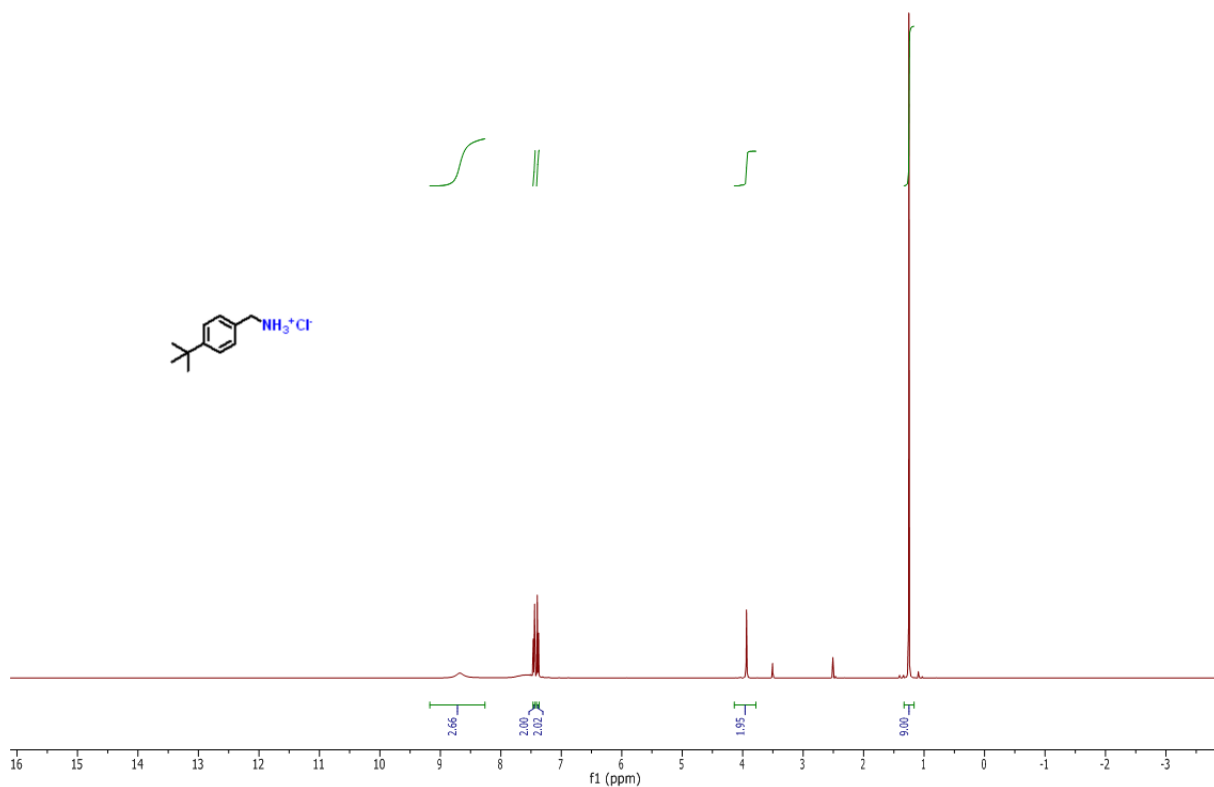
37.73

16.97



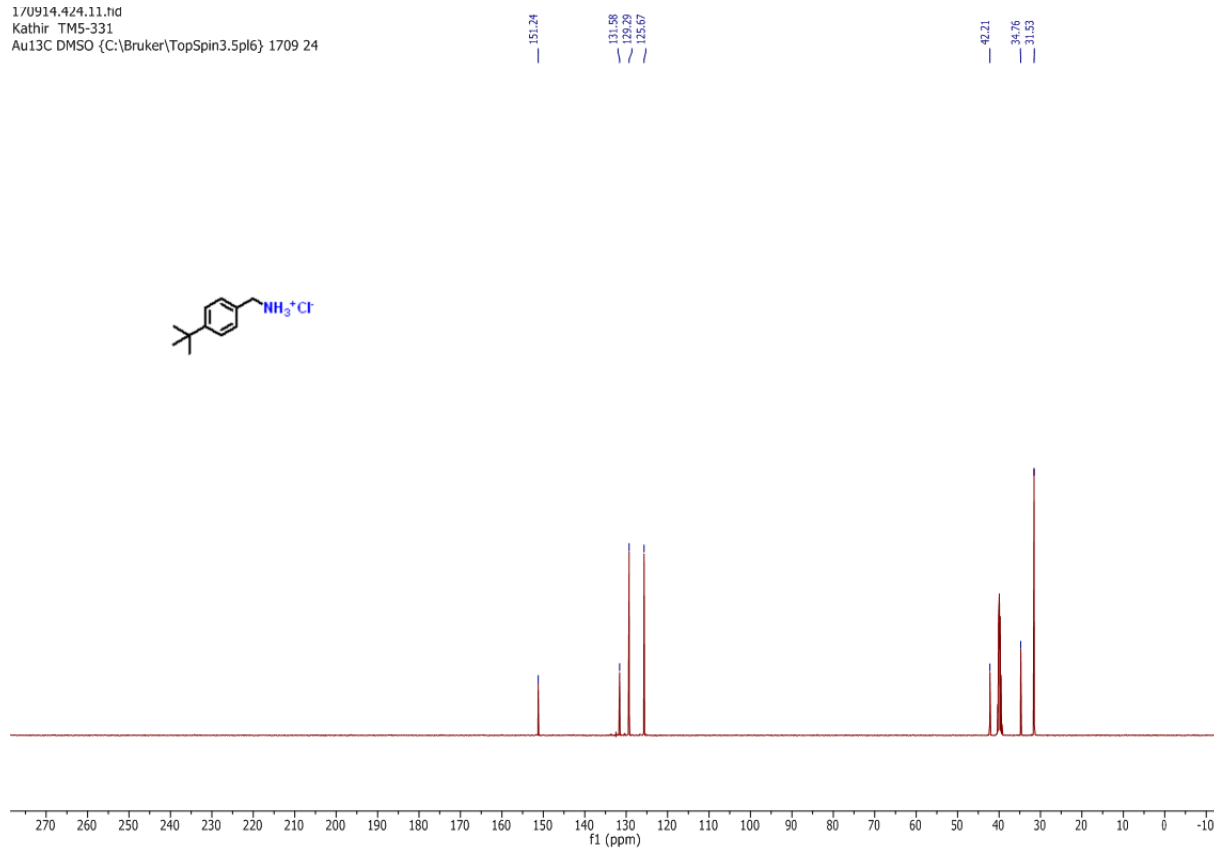
Supplementary Figure 23. ¹³C NMR spectrum

1/0914.424.10.nd
Kathir TMS-331
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 24

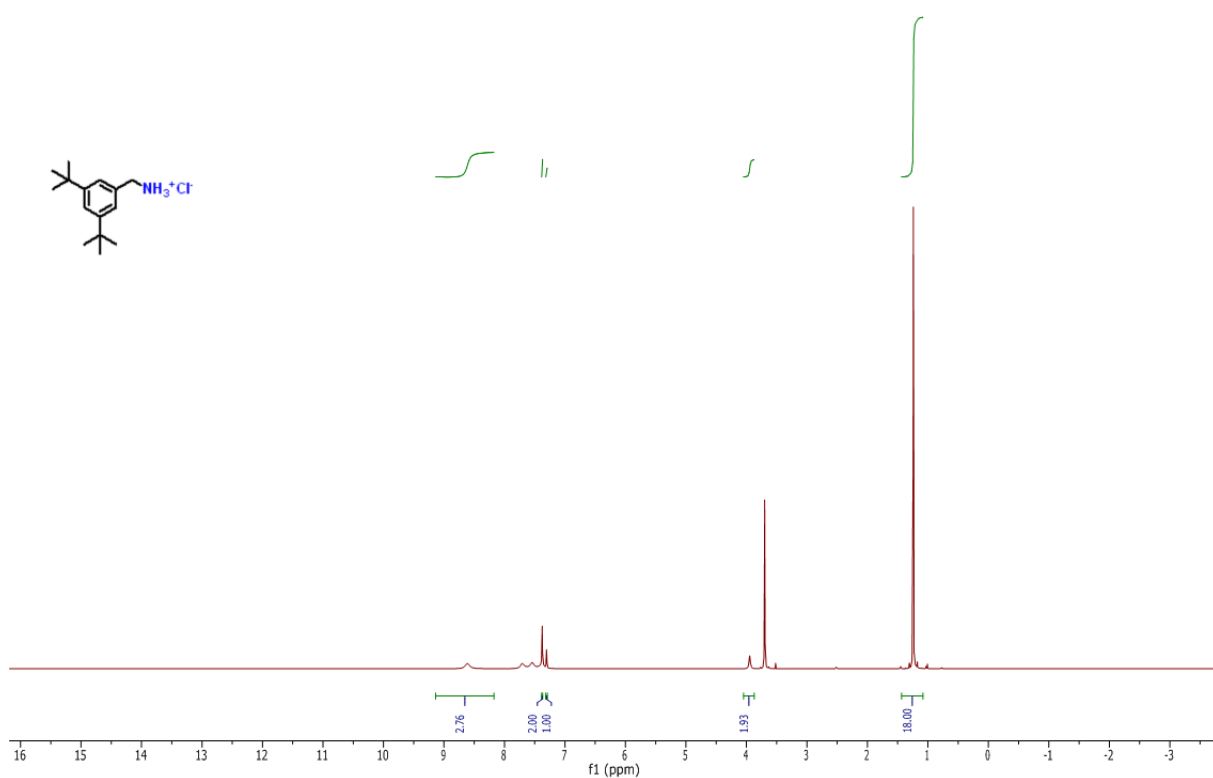


Supplementary Figure 24. ¹H NMR spectrum

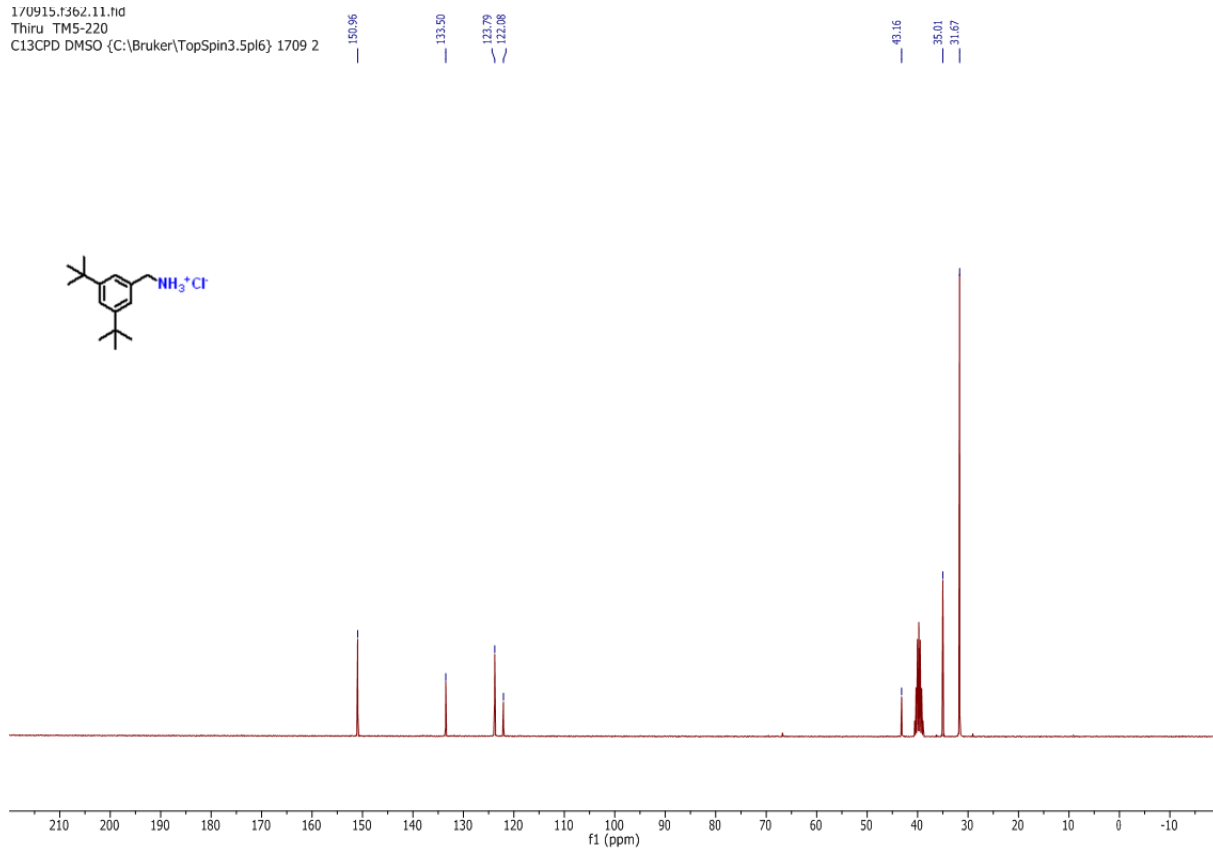
1/0914.424.11.nd
Kathir TMS-331
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 24



Supplementary Figure 25. ¹³C NMR spectrum

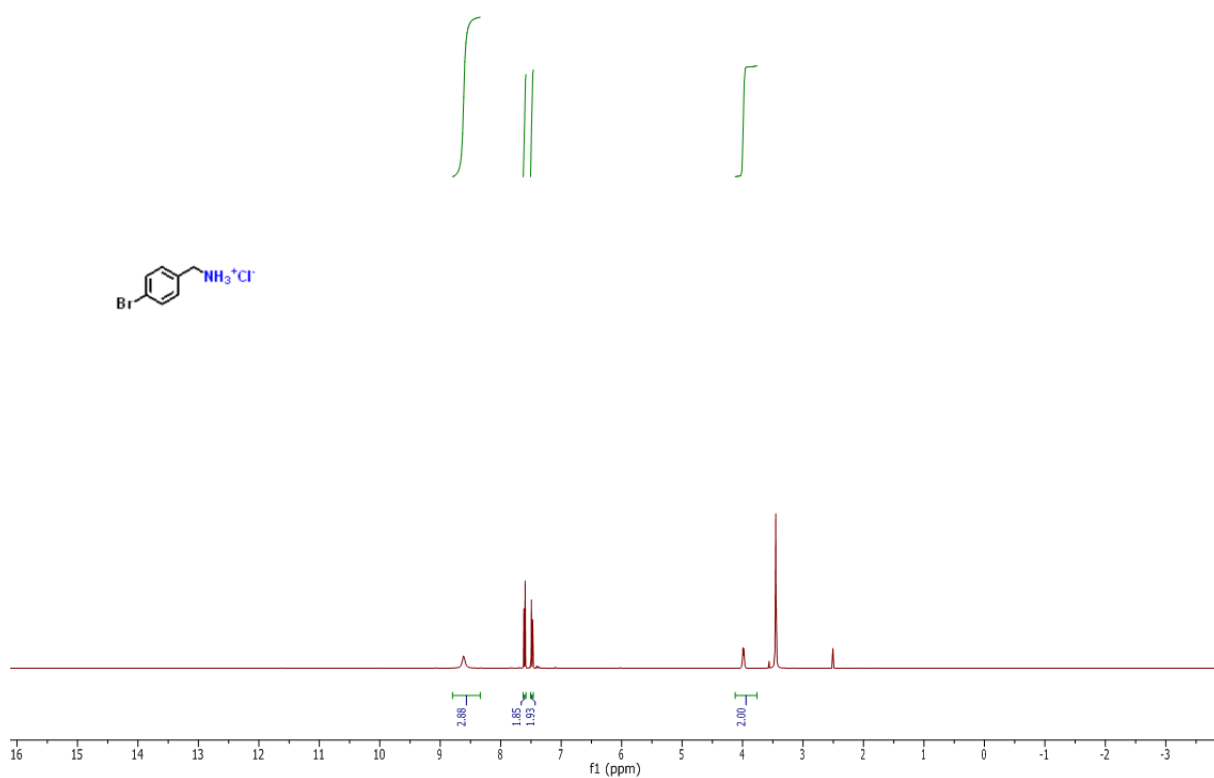
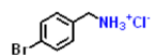


Supplementary Figure 26. ^1H NMR spectrum



Supplementary Figure 27. ^{13}C NMR spectrum

171023.406.10.nd
Thiru TMS-226
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1710 6



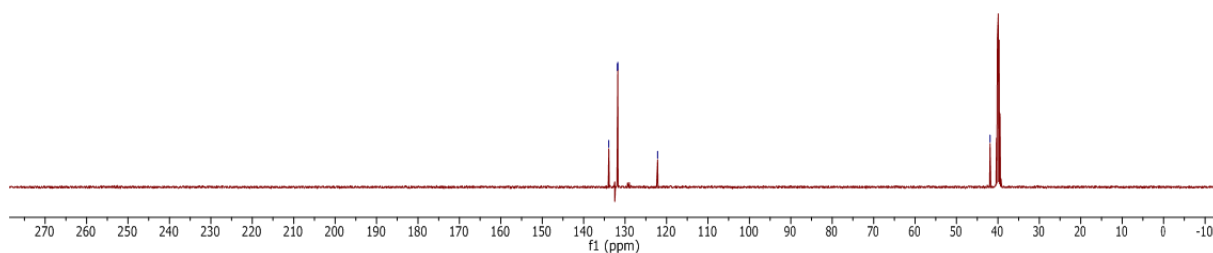
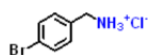
Supplementary Figure 28. ¹H NMR spectrum

171023.406.11.nd
Thiru TMS-226
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1710 6

133.94
131.85
131.77

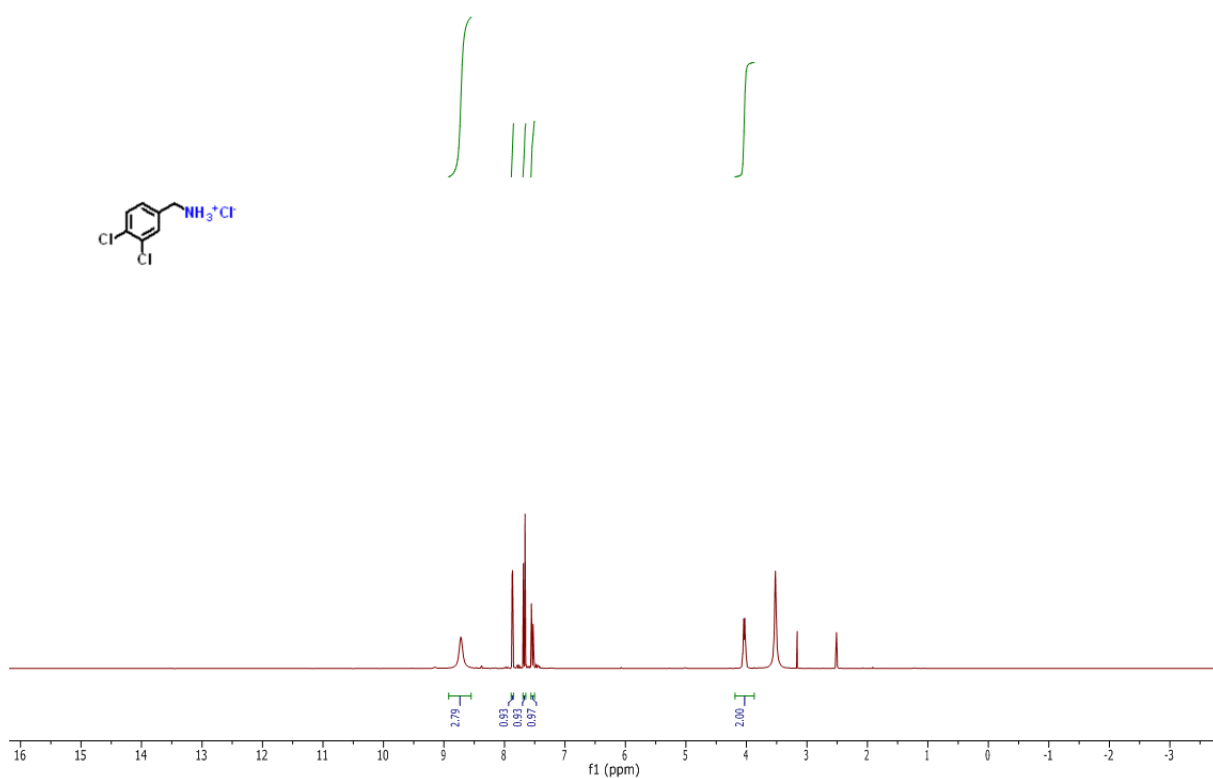
122.15

41.90



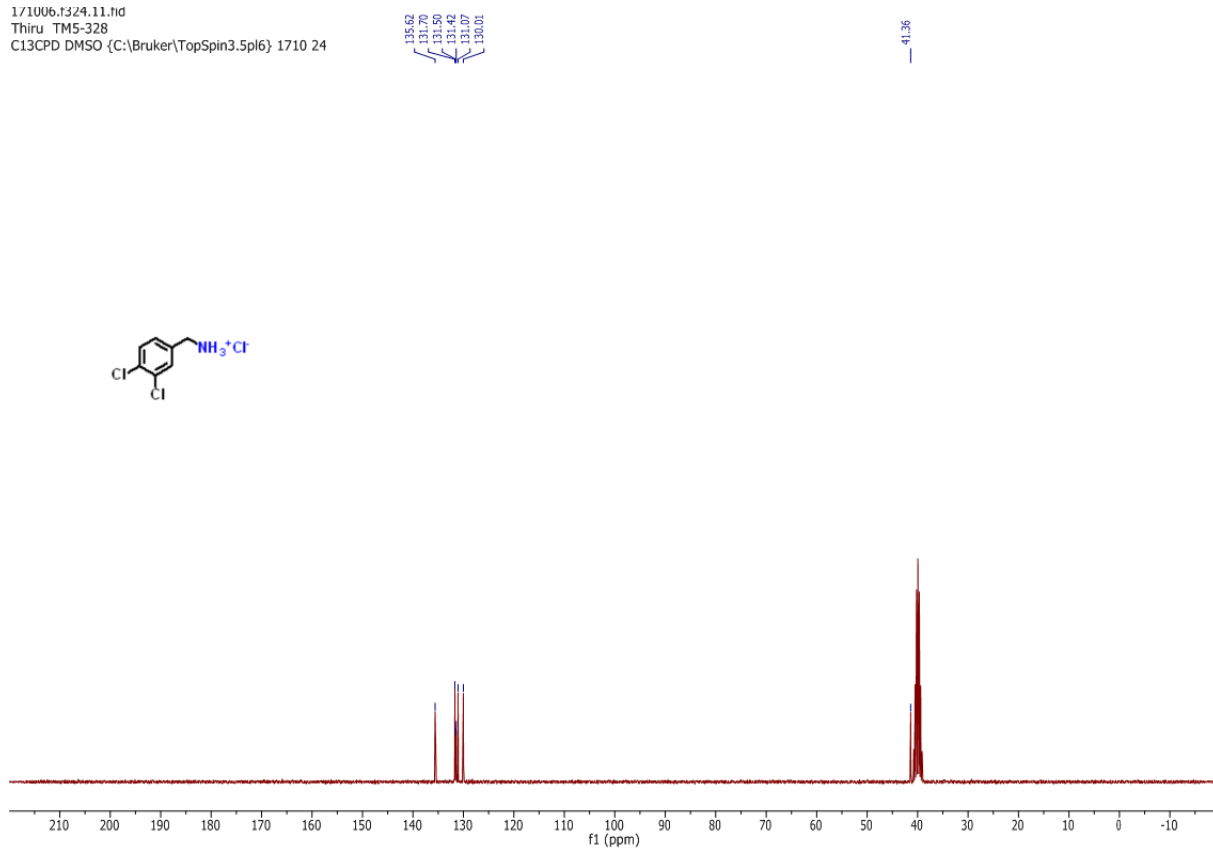
Supplementary Figure 29. ¹³C NMR spectrum

1/1006.f324.10.fid
Thiru TM5-328
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 24



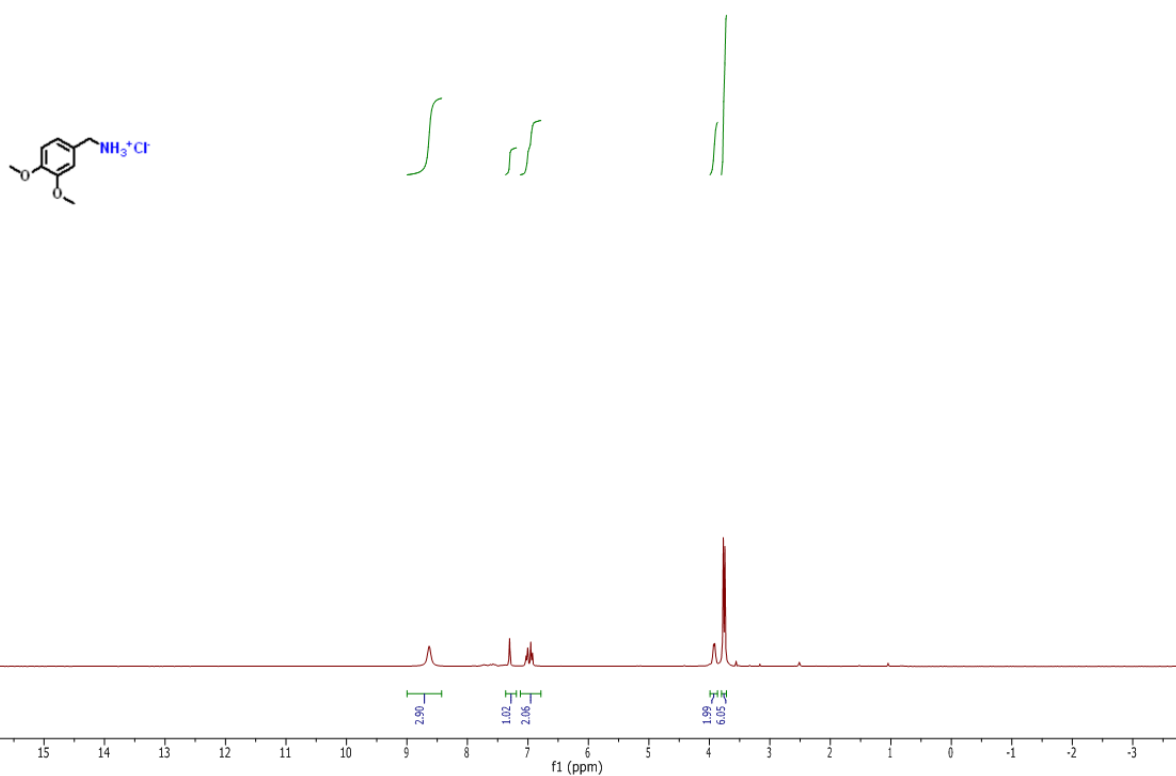
Supplementary Figure 30. ^1H NMR spectrum

1/1006.f324.11.fid
Thiru TM5-328
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 24



Supplementary Figure 31. ^{13}C NMR spectrum

170925.f330.10.fid
Thiru TM5-245
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 30

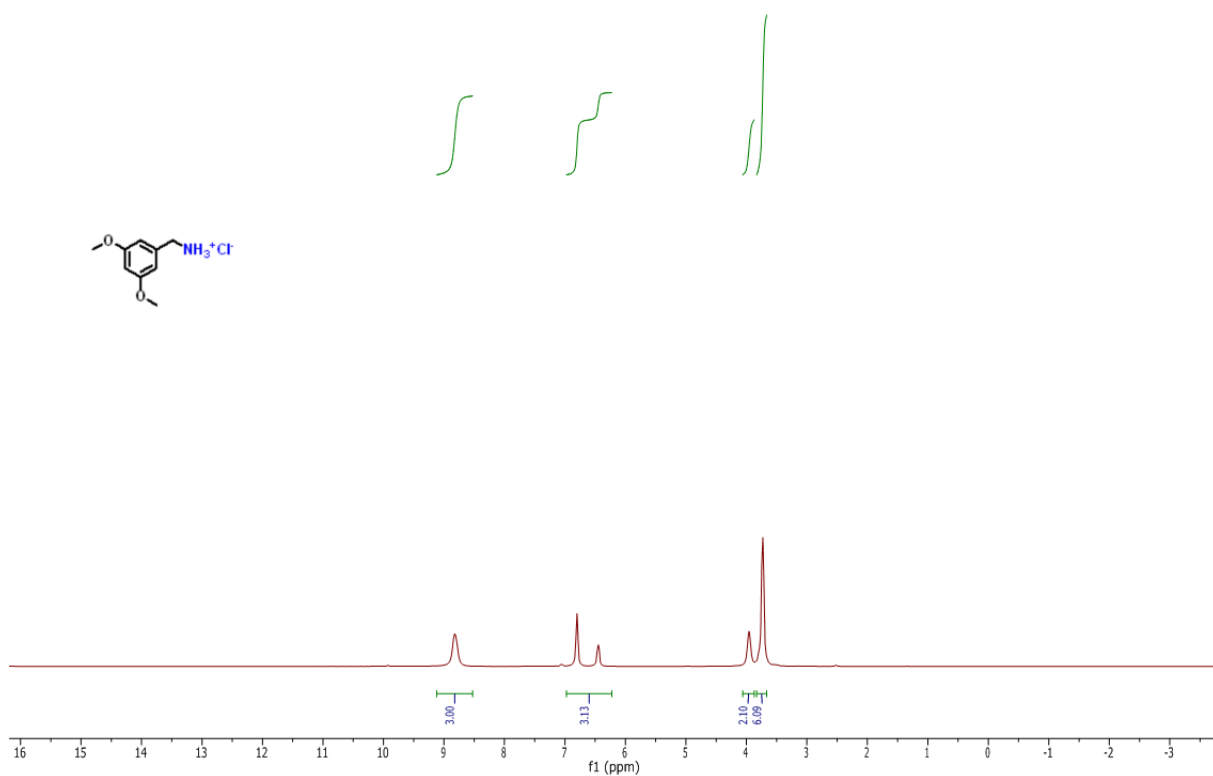


Supplementary Figure 32. ¹H NMR spectrum

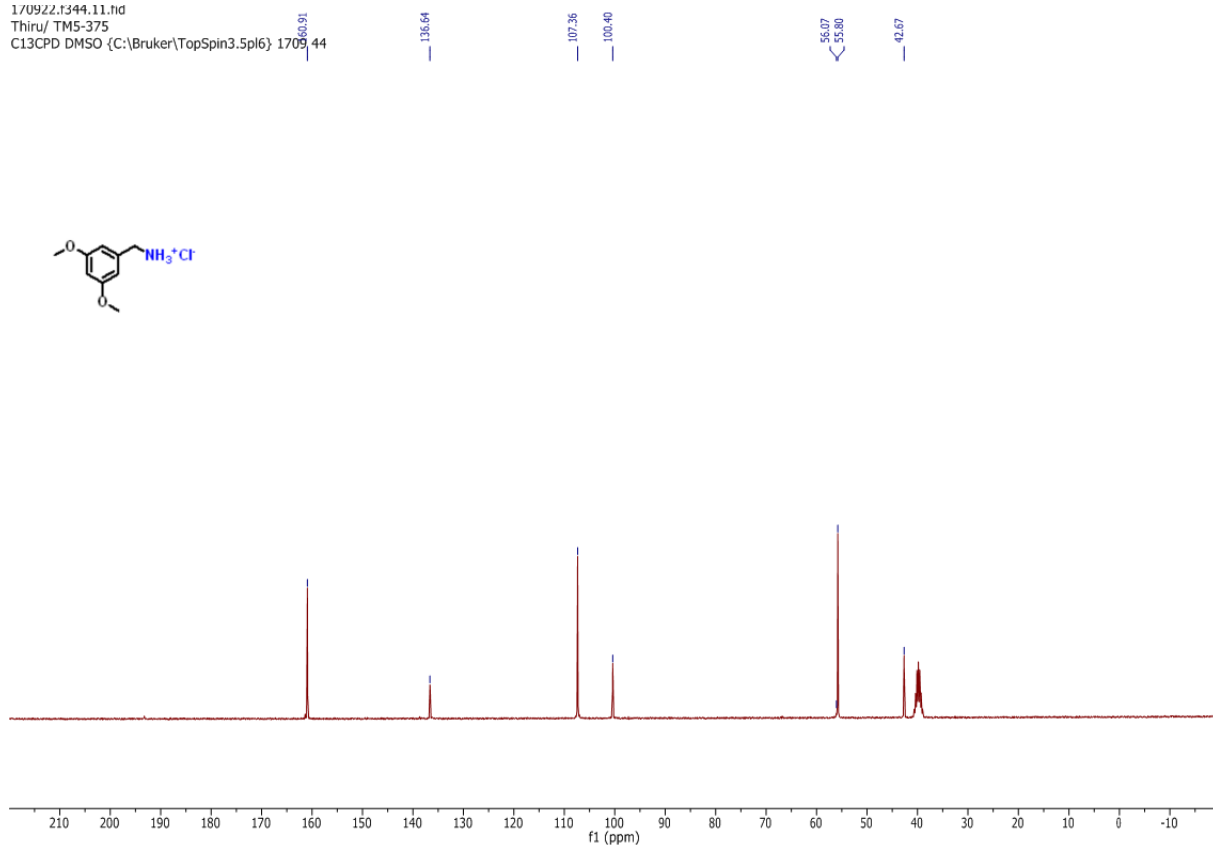
170925.f330.11.fid
Thiru TM5-245
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 30



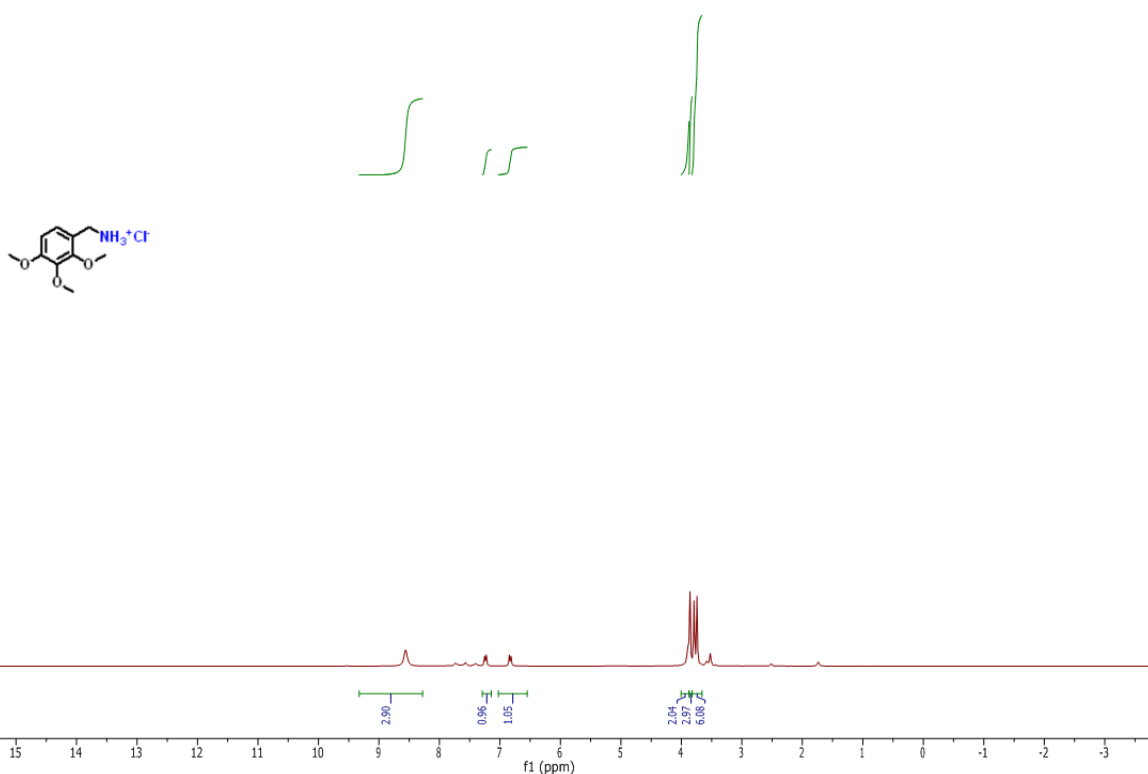
Supplementary Figure 33. ¹³C NMR spectrum



Supplementary Figure 34. ¹H NMR spectrum



Supplementary Figure 35. ¹³C NMR spectrum

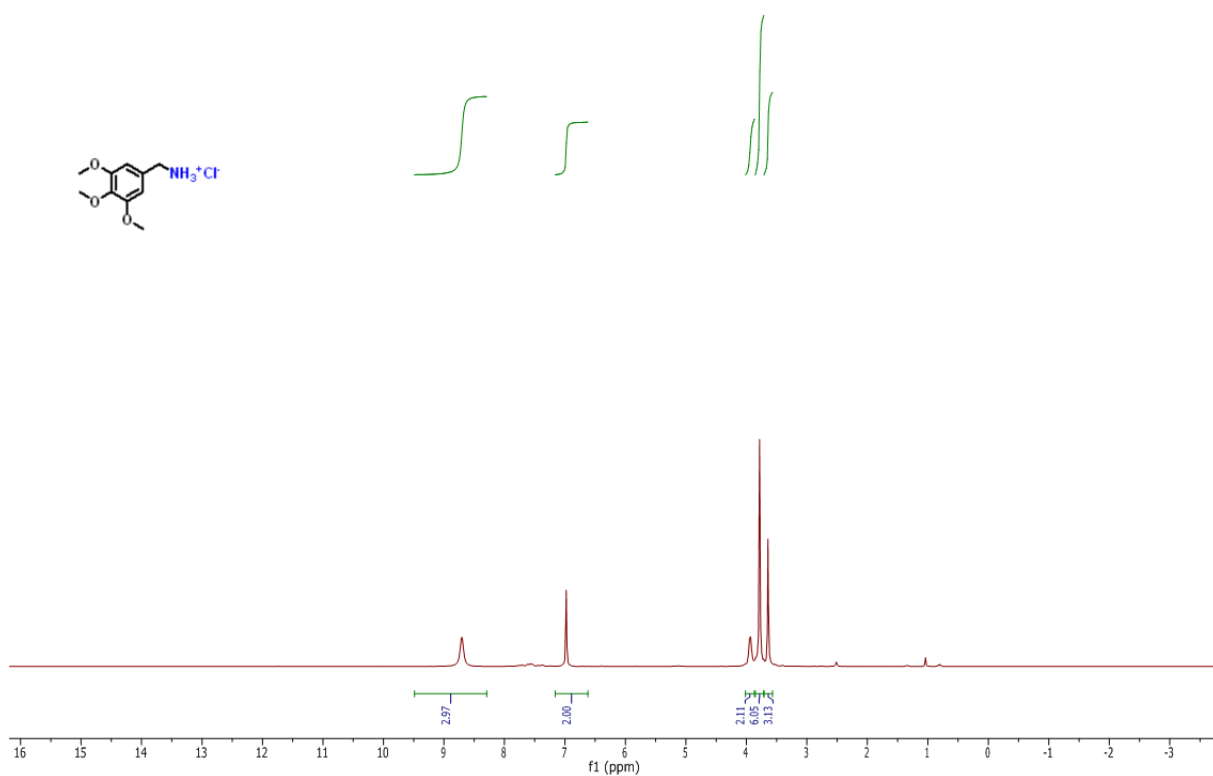


Supplementary Figure 36. ¹H NMR spectrum



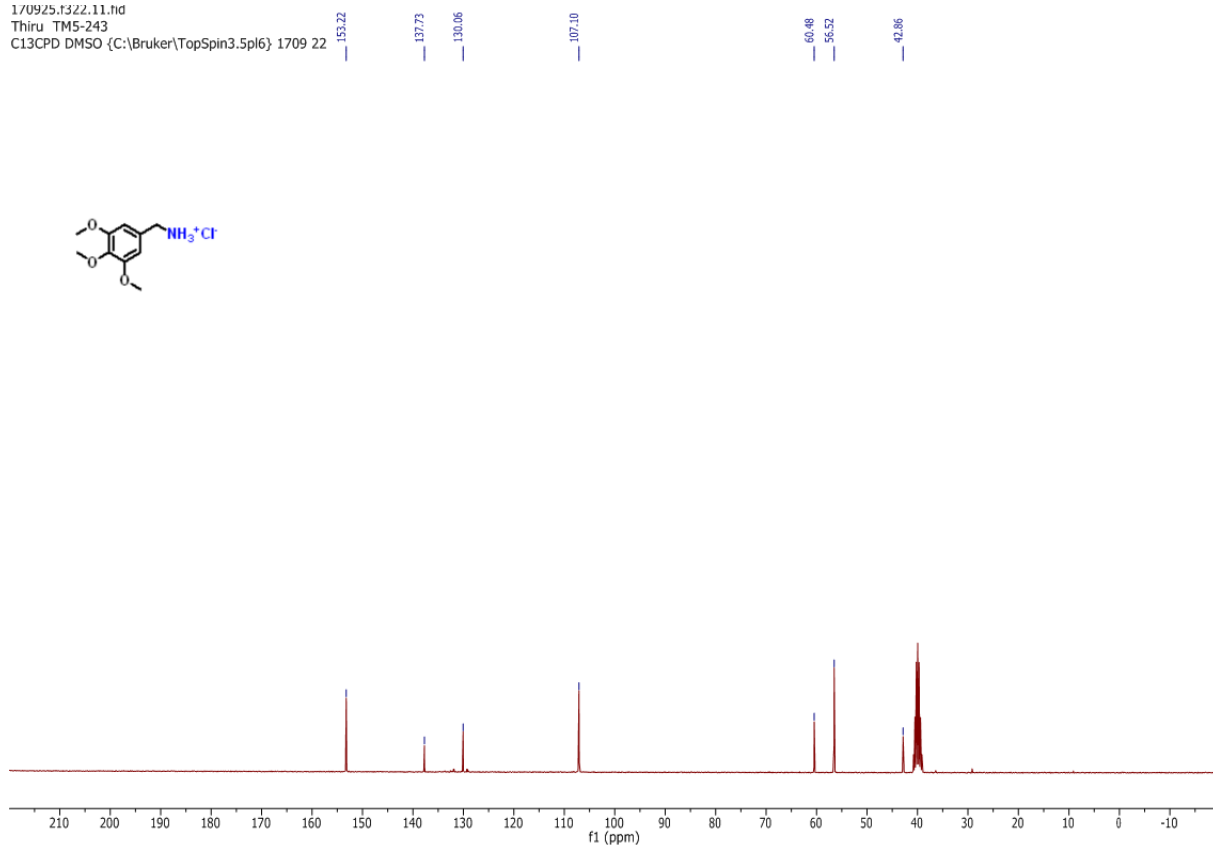
Supplementary Figure 37. ¹³C NMR spectrum

170925.f322.10.fid
Thiru TM5-243
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 22



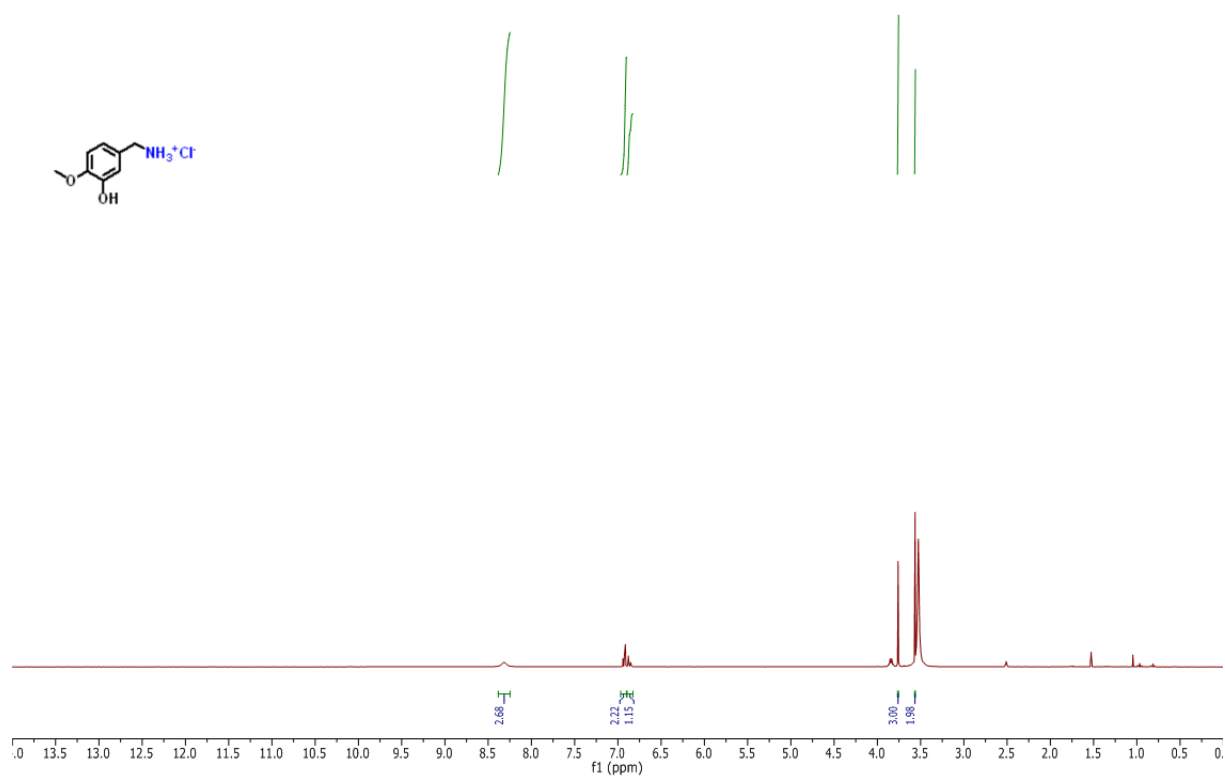
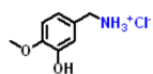
Supplementary Figure 38. ¹H NMR spectrum

170925.f322.11.fid
Thiru TM5-243
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 22



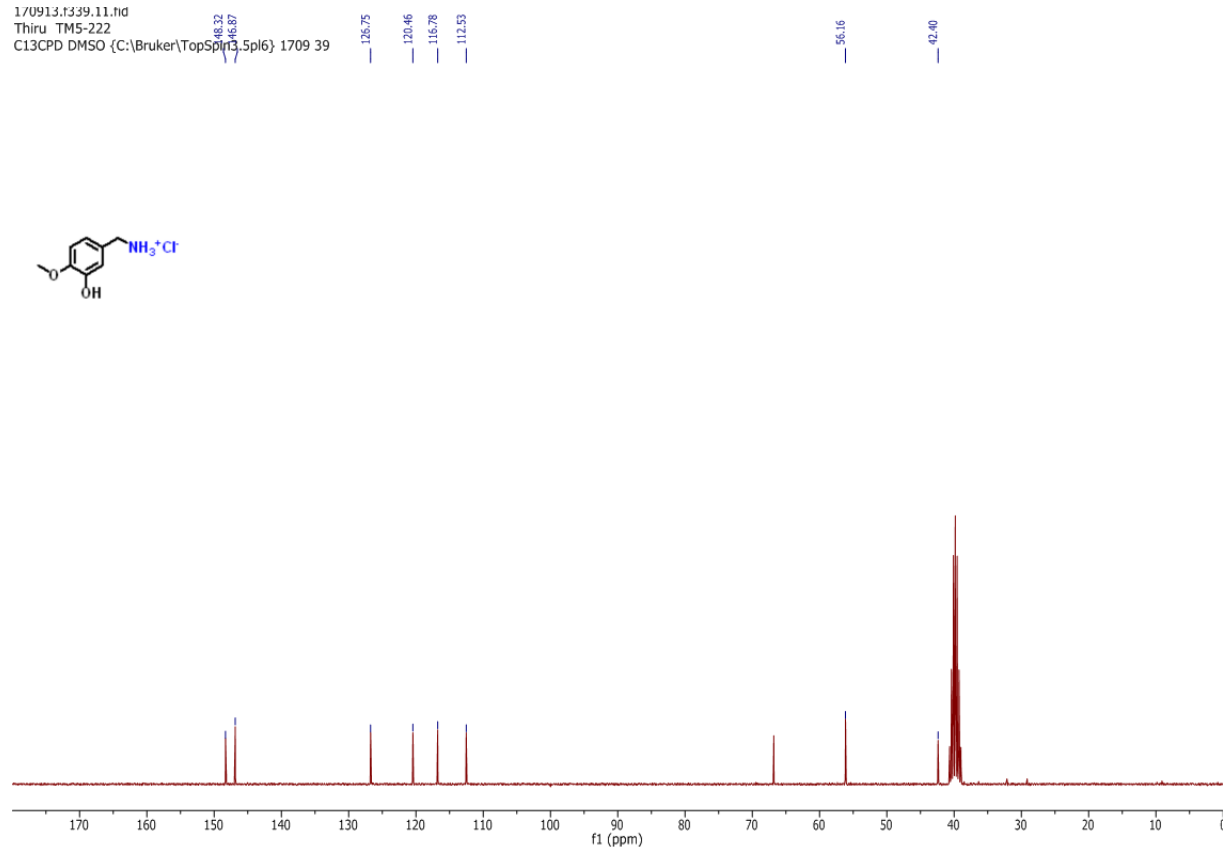
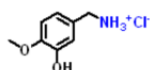
Supplementary Figure 39. ¹³C NMR spectrum

170913.1339.10.fid
Thiru TM5-222
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 39



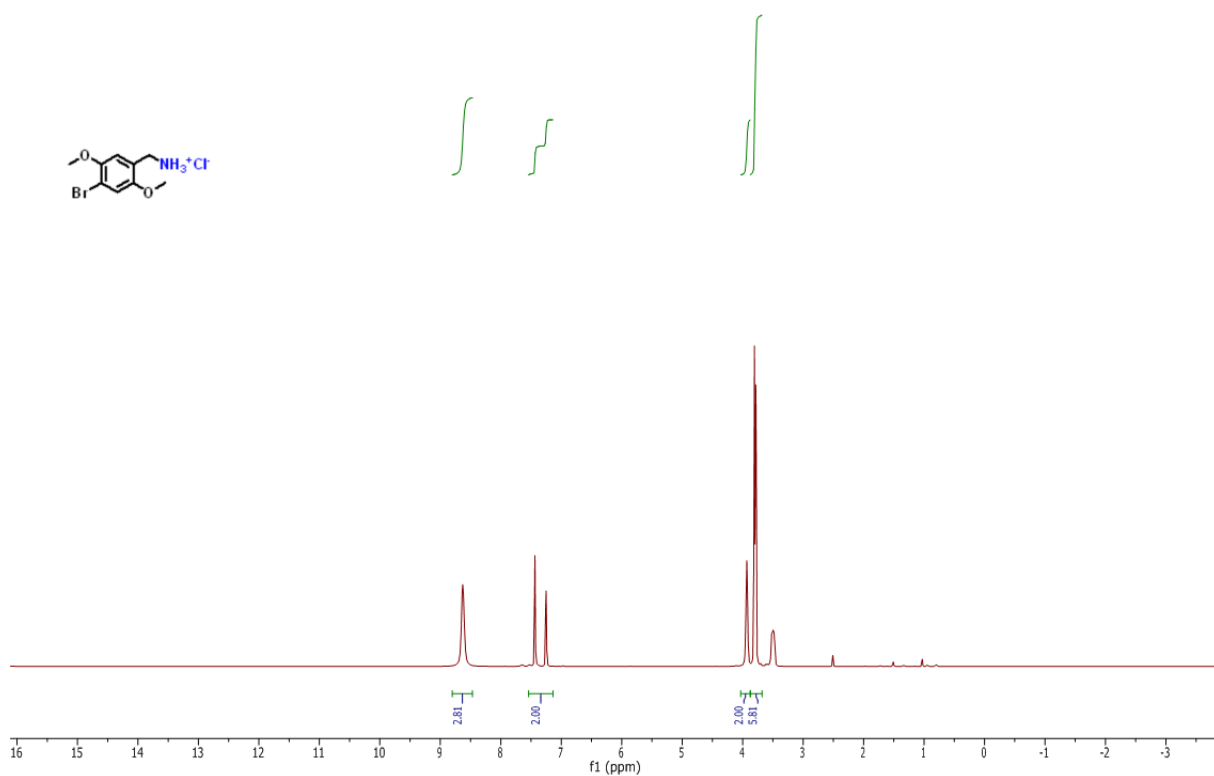
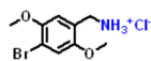
Supplementary Figure 40. ¹H NMR spectrum

170913.1339.11.fid
Thiru TM5-222
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 39



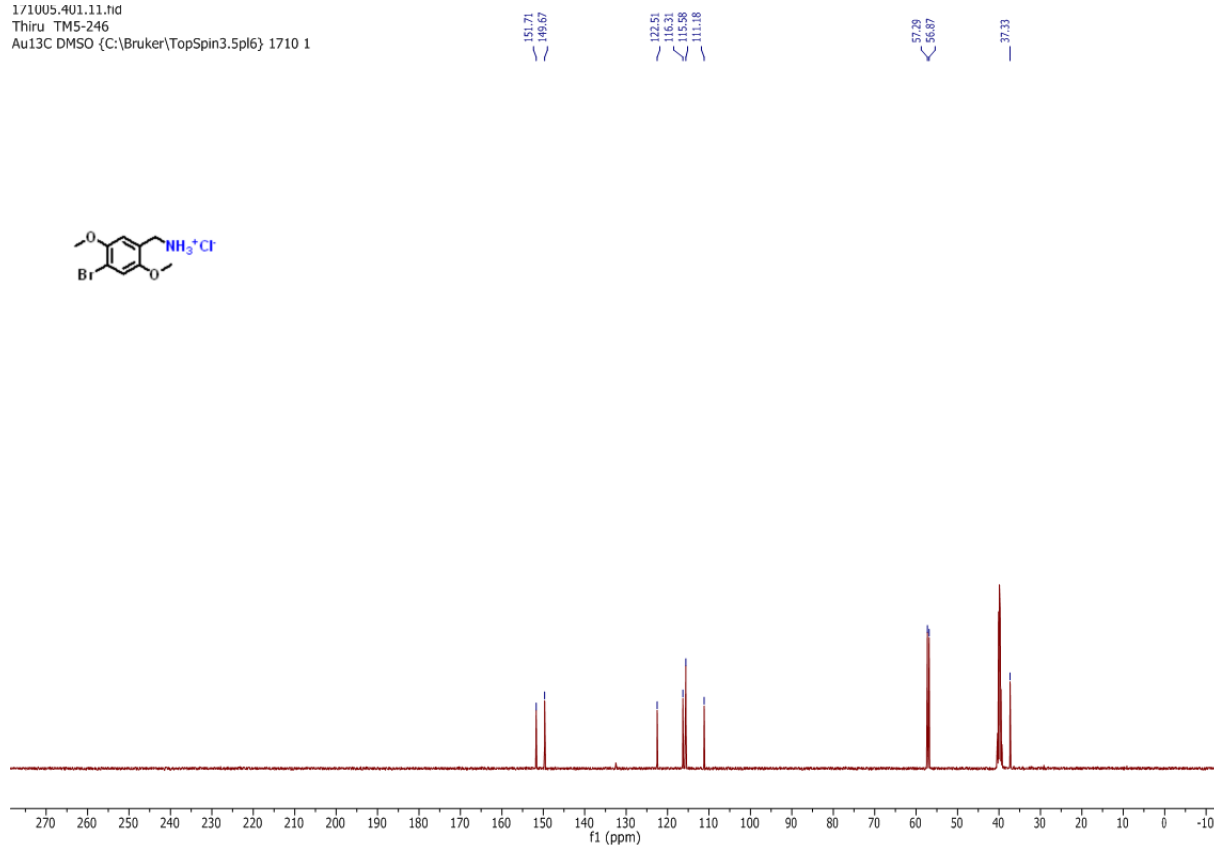
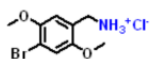
Supplementary Figure 41. ¹³C NMR spectrum

1/1005.401.10.nd
Thiru TMS-246
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1710 1



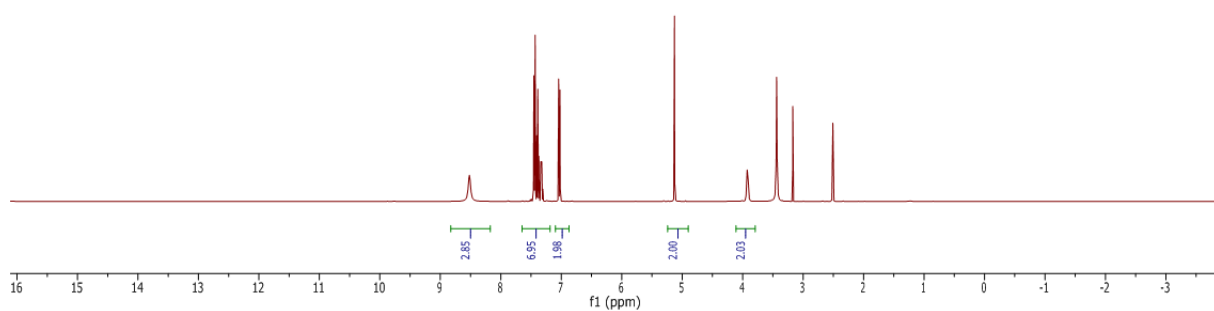
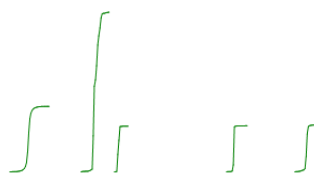
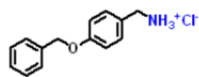
Supplementary Figure 42. ¹H NMR spectrum

1/1005.401.11.nd
Thiru TMS-246
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1710 1



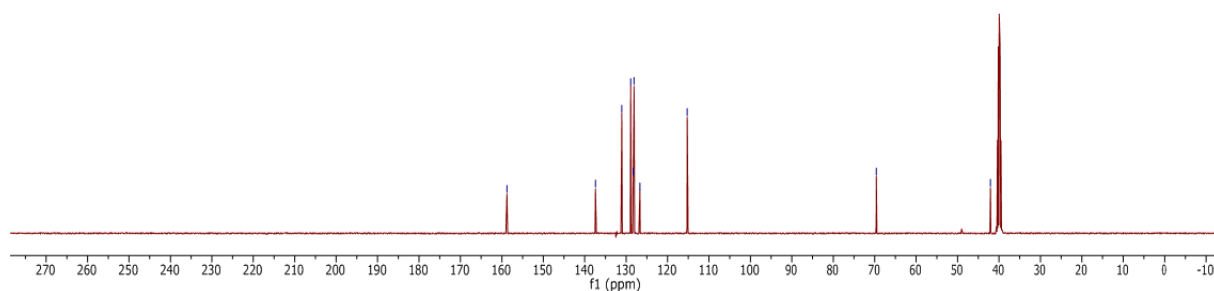
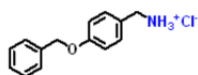
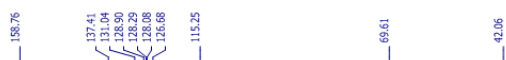
Supplementary Figure 43. ¹³C NMR spectrum

1/0914.415.10.nd
Kathir TMS-324
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 15



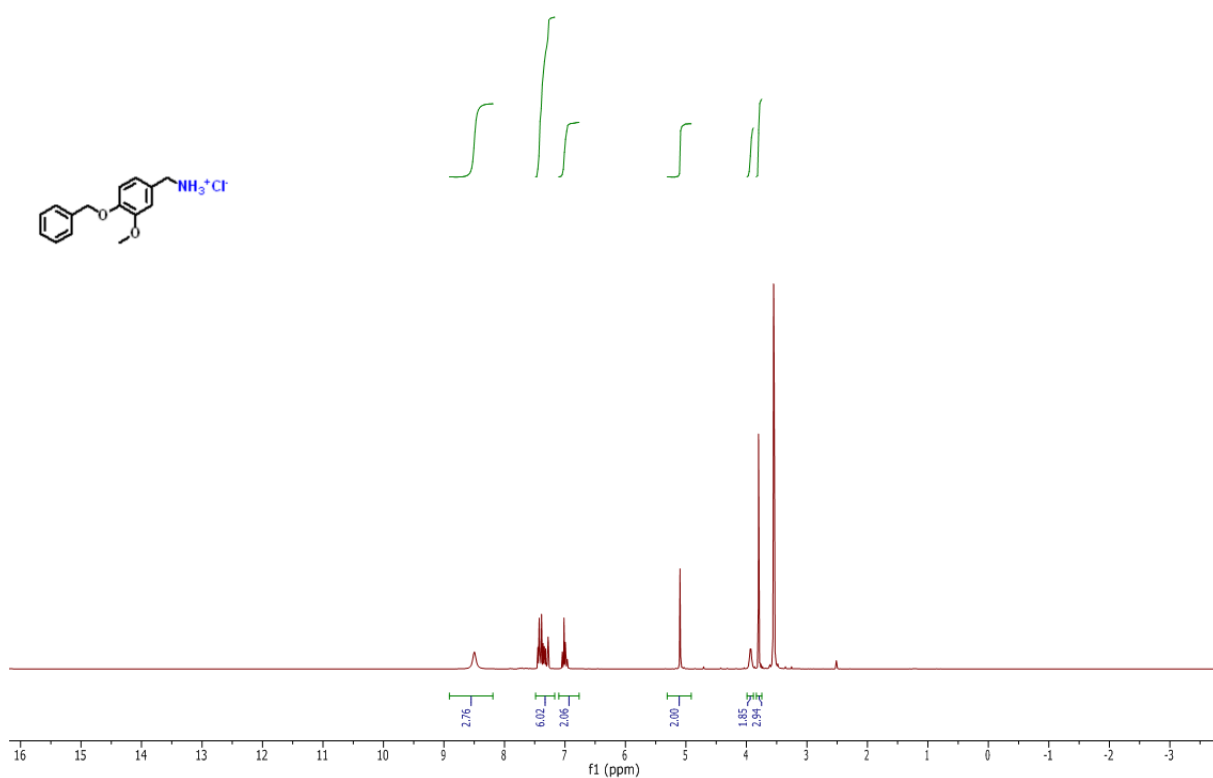
Supplementary Figure 44. ^1H NMR spectrum

1/0914.415.11.nd
Kathir TMS-324
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 15



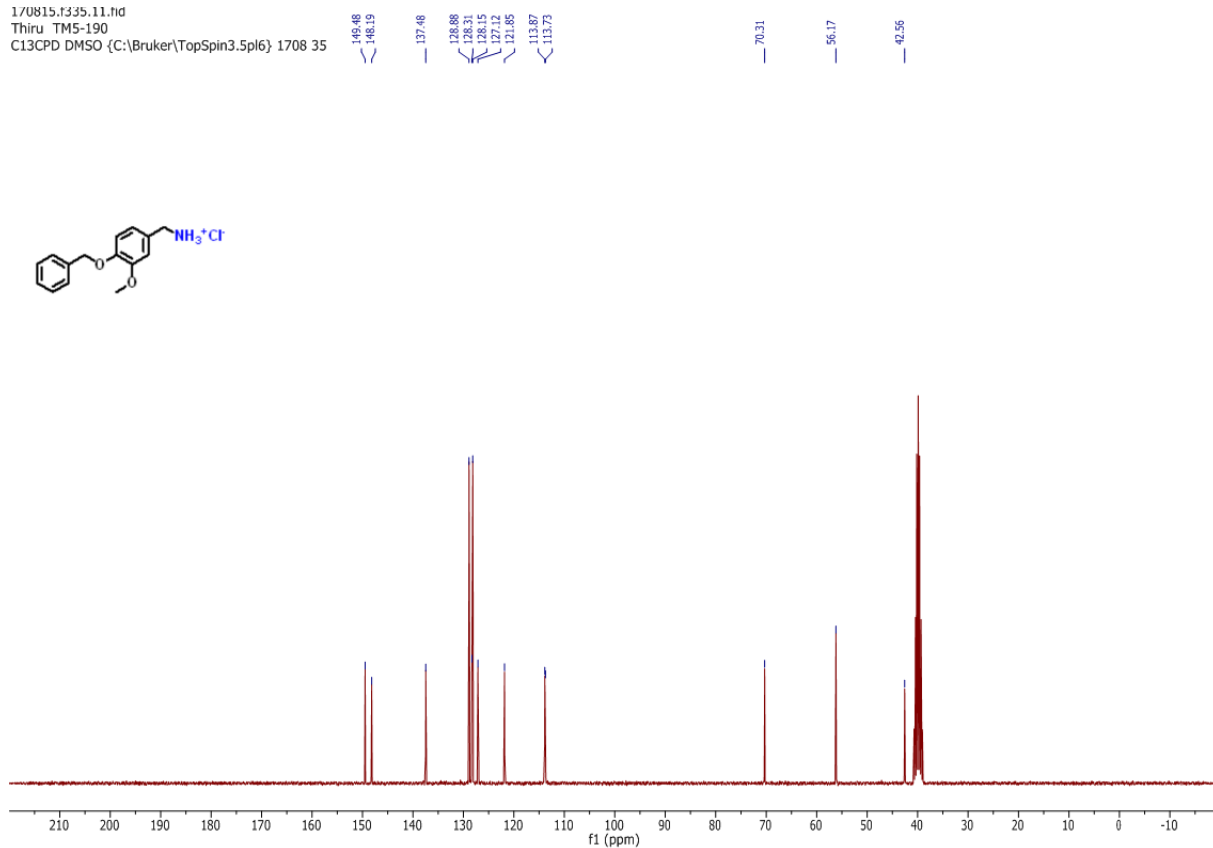
Supplementary Figure 45. ^{13}C NMR spectrum

1/0815.1335.10.fid
Thiru TM5-190
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1708 35



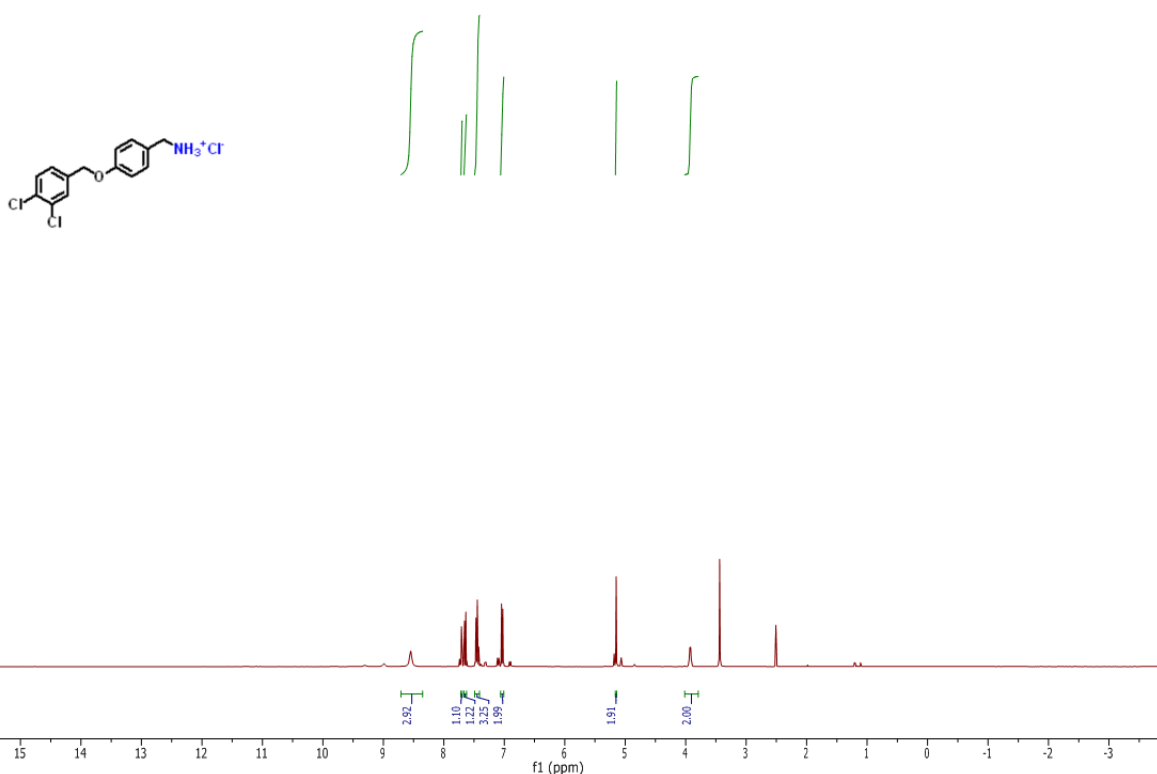
Supplementary Figure 46. ¹H NMR spectrum

1/0815.1335.11.fid
Thiru TM5-190
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1708 35



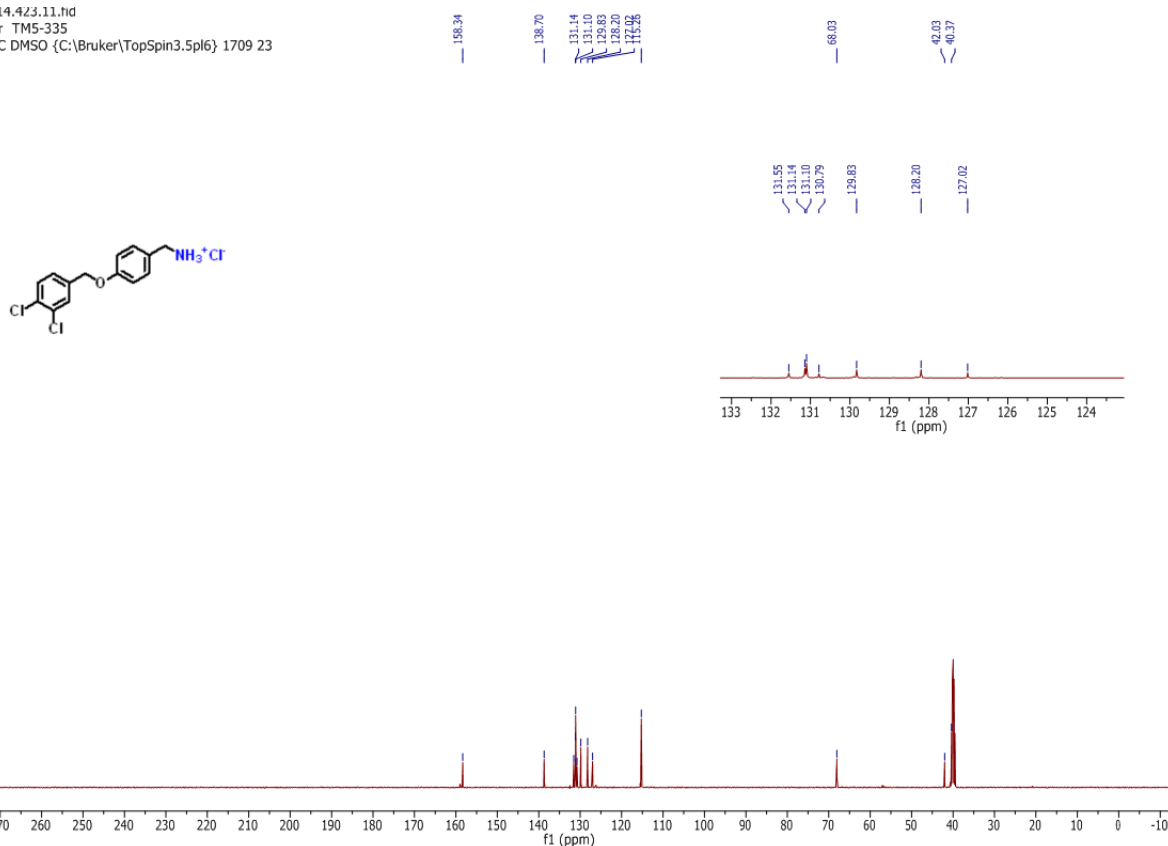
Supplementary Figure 47. ¹³C NMR spectrum

170914.423.10.nd
Kathir TMS-335
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 23



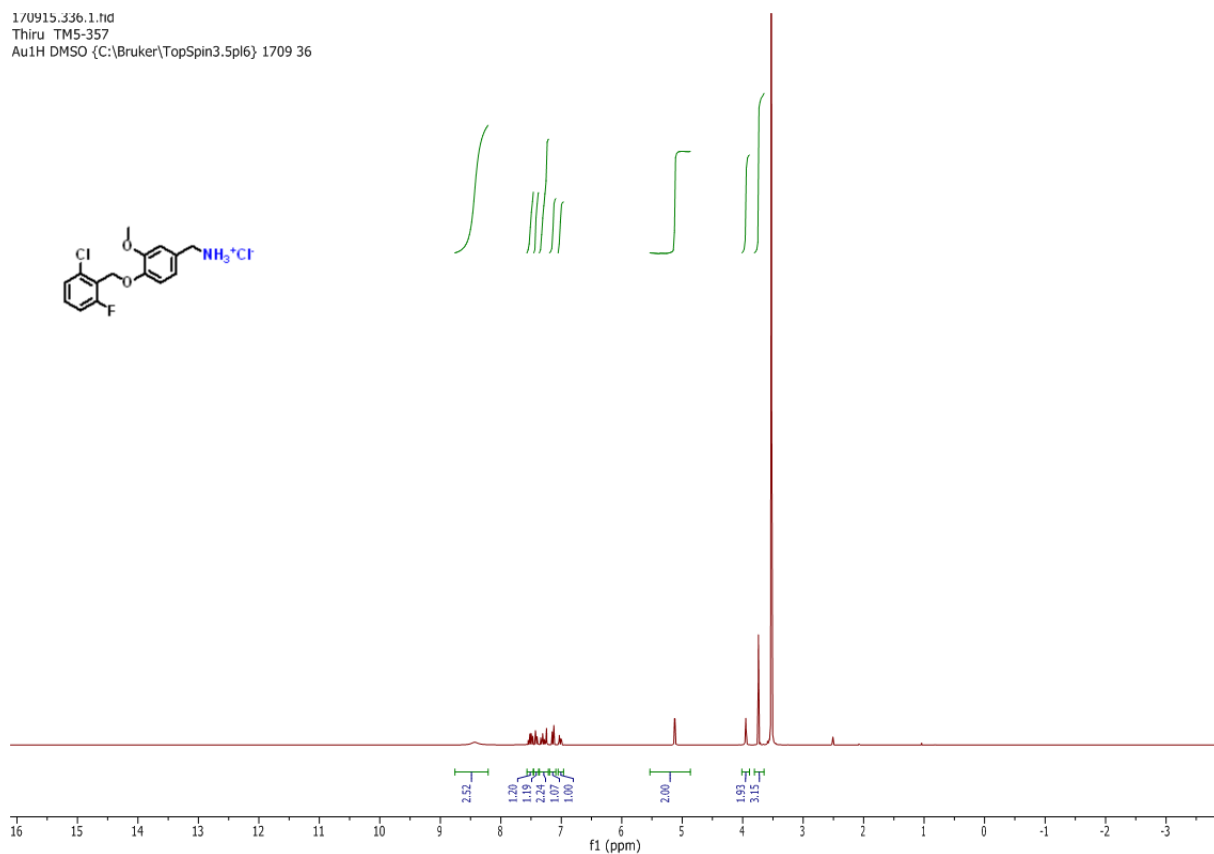
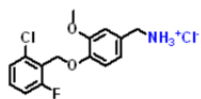
Supplementary Figure 48. ¹H NMR spectrum

170914.423.11.nd
Kathir TMS-335
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 23



Supplementary Figure 49. ¹³C NMR spectrum

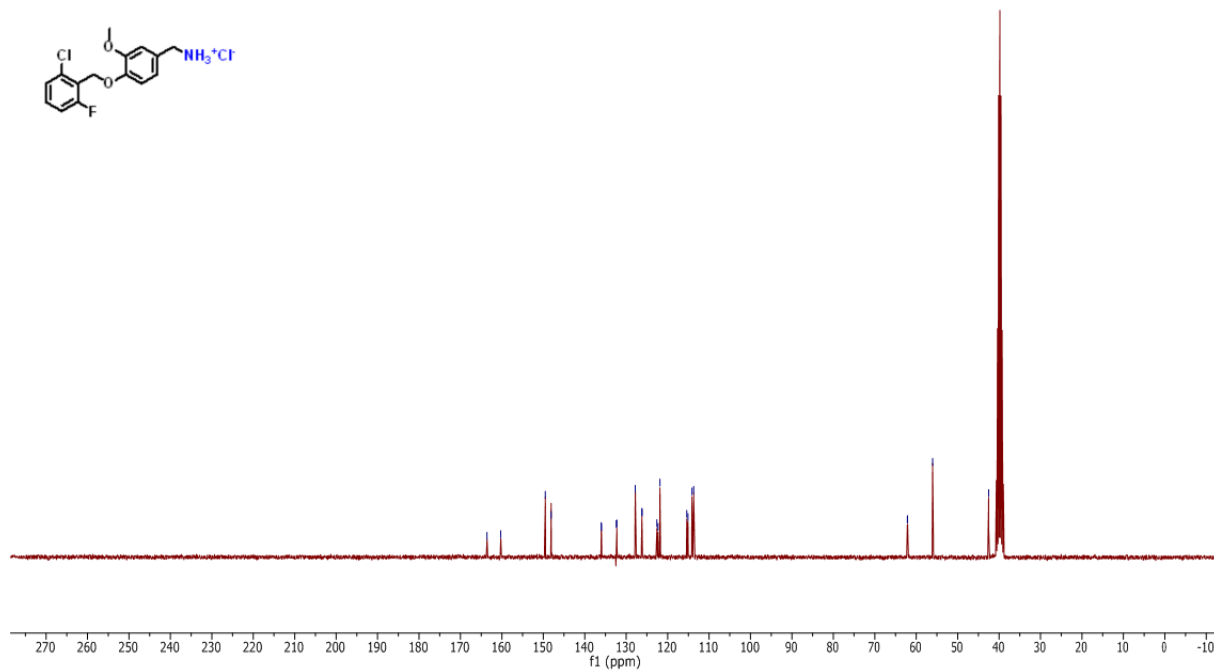
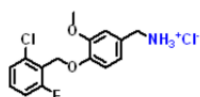
170915.336.1.hd
Thiru TMS-357
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 36



Supplementary Figure 50. ¹H NMR spectrum

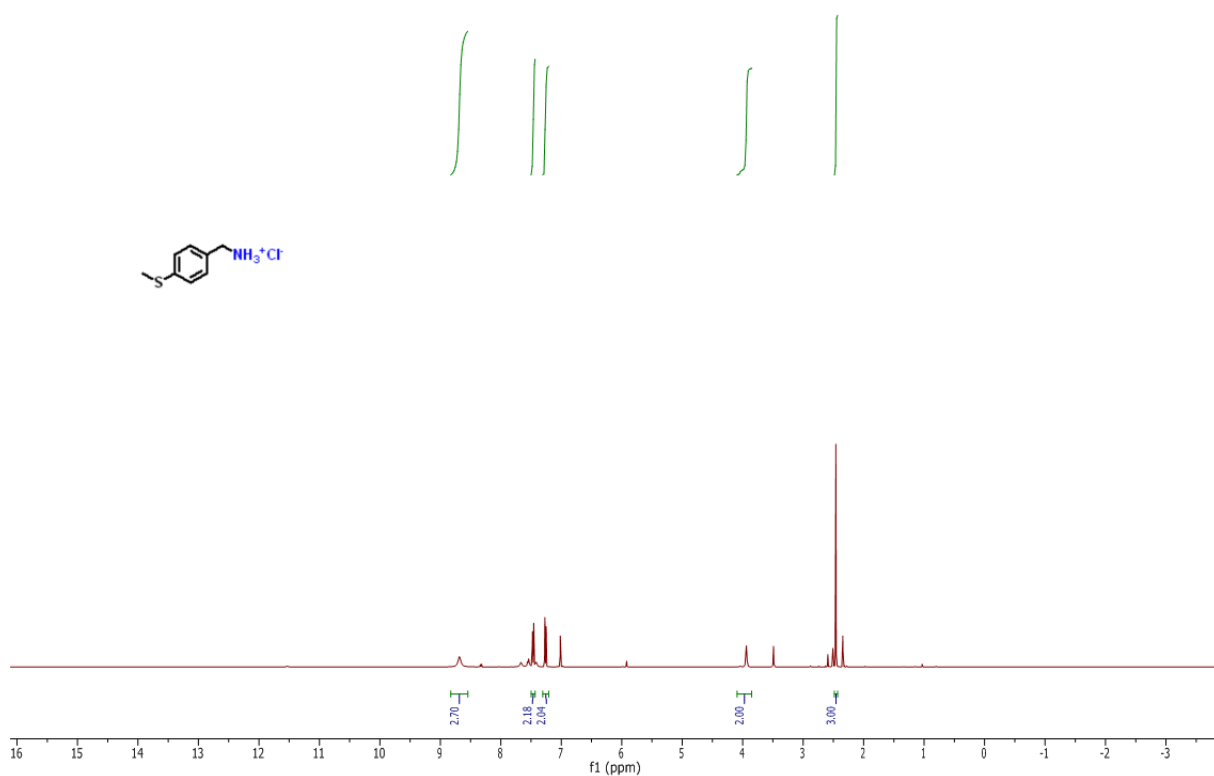
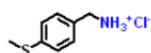
170915.336.2.hd
Thiru TMS-357
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 36

163.59 160.28 149.51 148.10 136.02 135.95 132.38 129.75 127.88 126.20 126.16 122.58 122.34 121.86 115.37 114.68 114.12 113.69 62.14 62.08 56.05 42.52



Supplementary Figure 51. ¹³C NMR spectrum

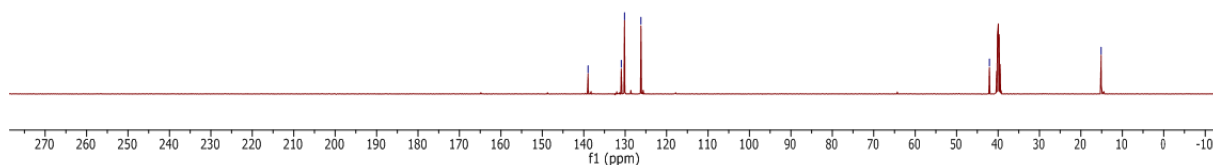
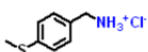
1/0914.421.10.nd
Kathir TMS-329
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 21



Supplementary Figure 52. ¹H NMR spectrum

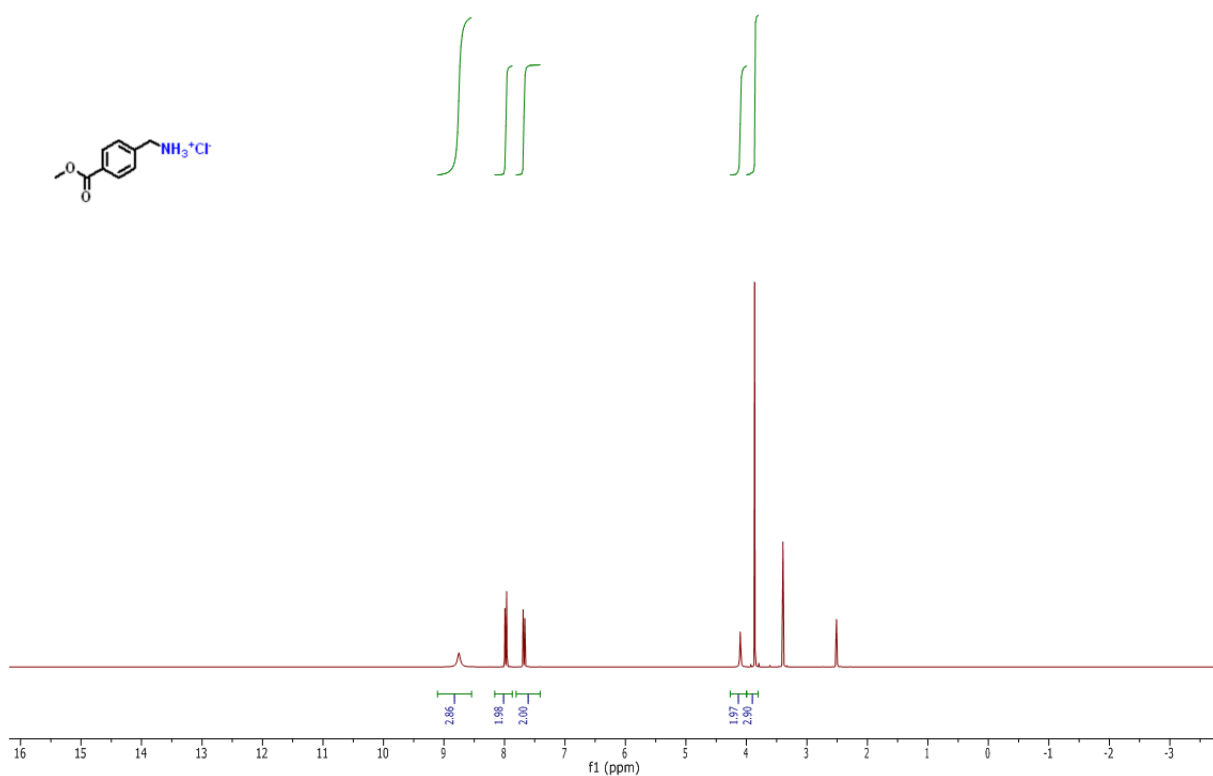
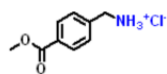
1/0914.421.11.nd
Kathir TMS-329
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 21

138.95
130.94
130.18
126.19
42.08
15.11



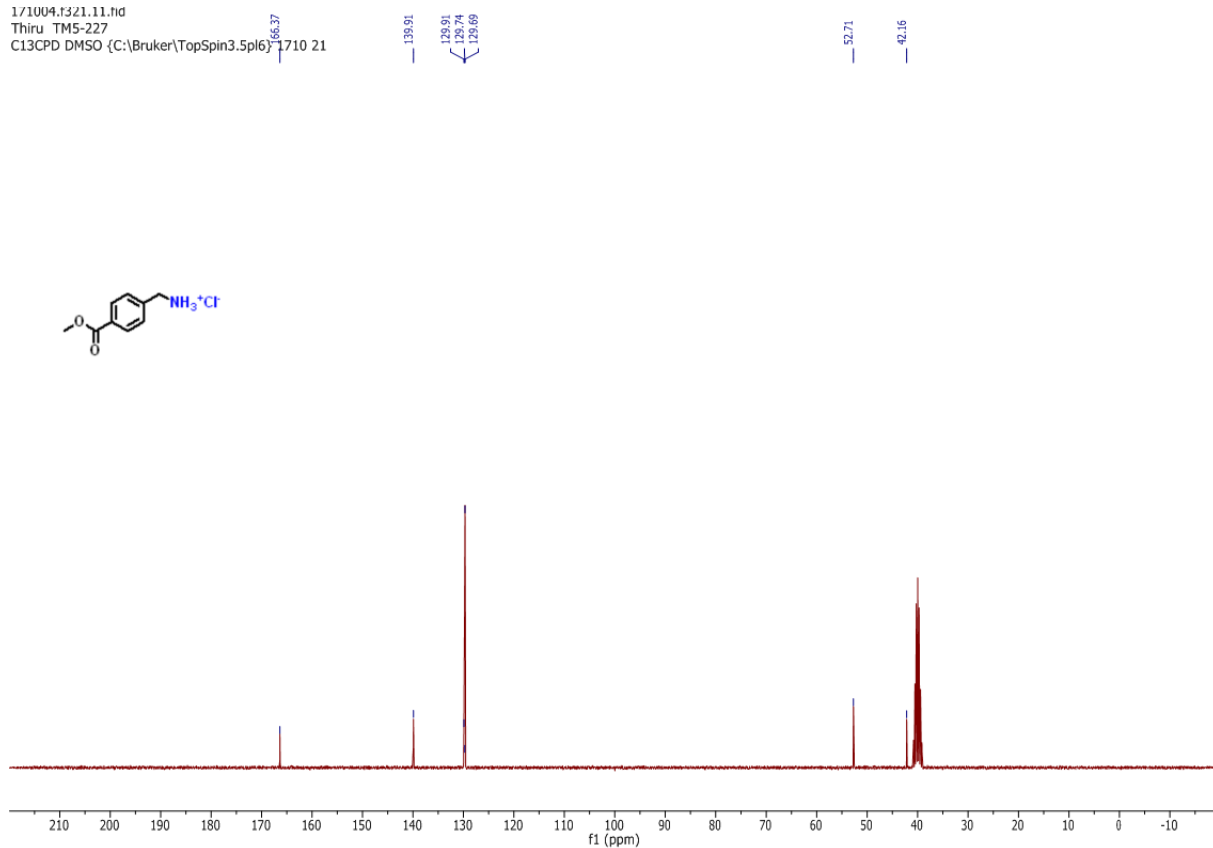
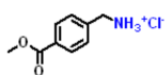
Supplementary Figure 53. ¹³C NMR spectrum

1/1004.f321.10.fid
Thiru TM5-227
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 21



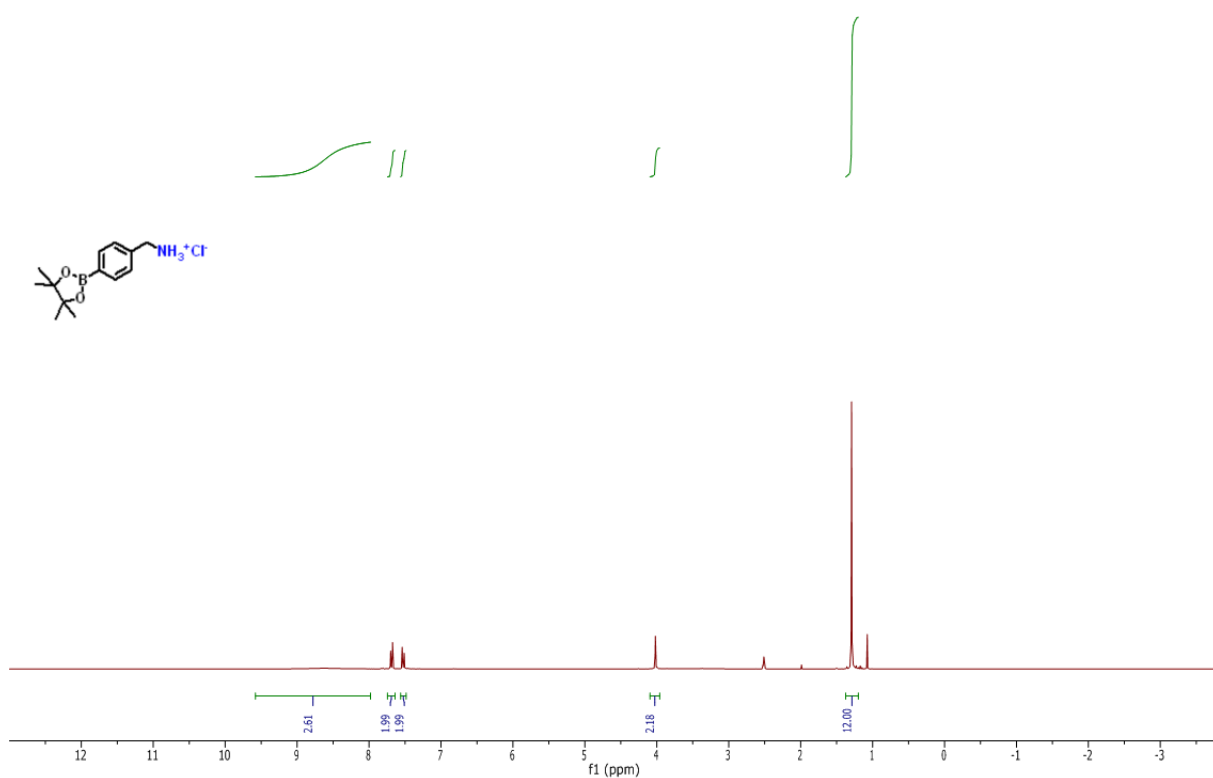
Supplementary Figure 54. ¹H NMR spectrum

1/1004.f321.11.fid
Thiru TM5-227
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 21



Supplementary Figure 55. ¹³C NMR spectrum

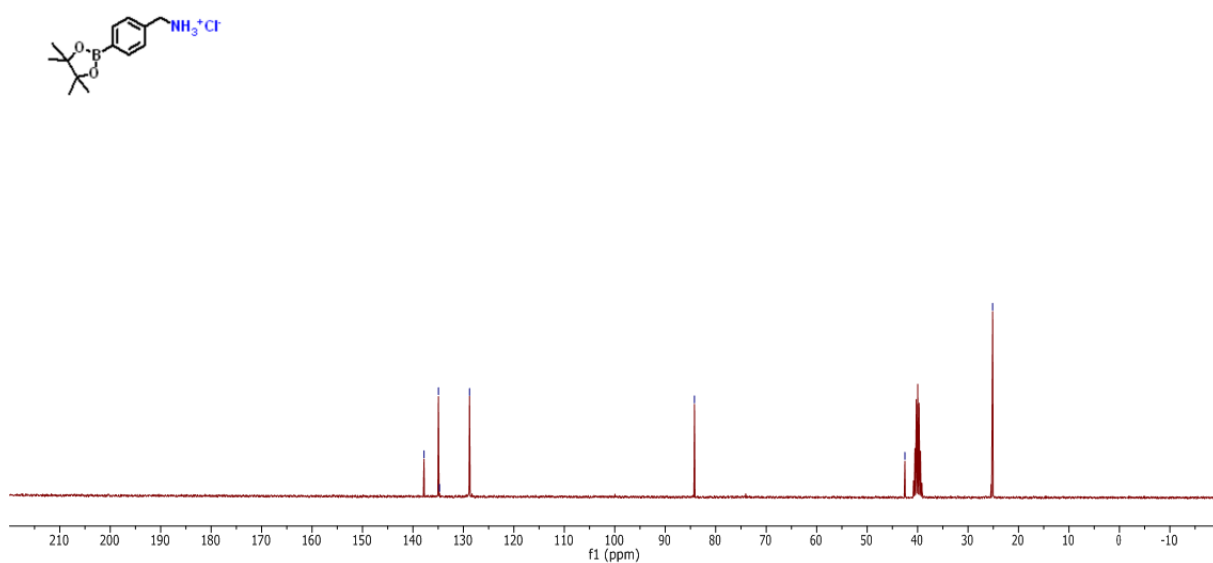
1/1004.f317.10.fid
Thiru_TMS-194
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 17



Supplementary Figure 56. ¹H NMR spectrum

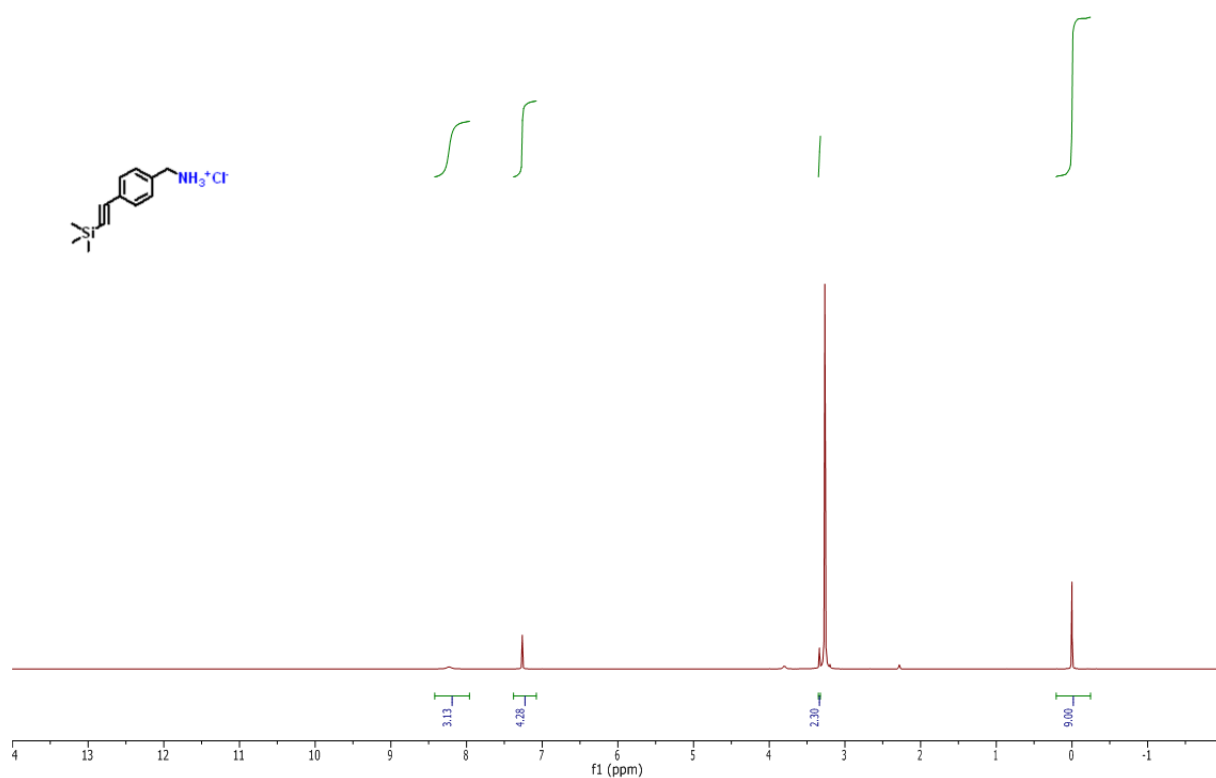
1/1004.f317.11.fid
Thiru_TMS-194
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 17

137.82
134.95
134.73
128.79
84.21
42.52
25.13



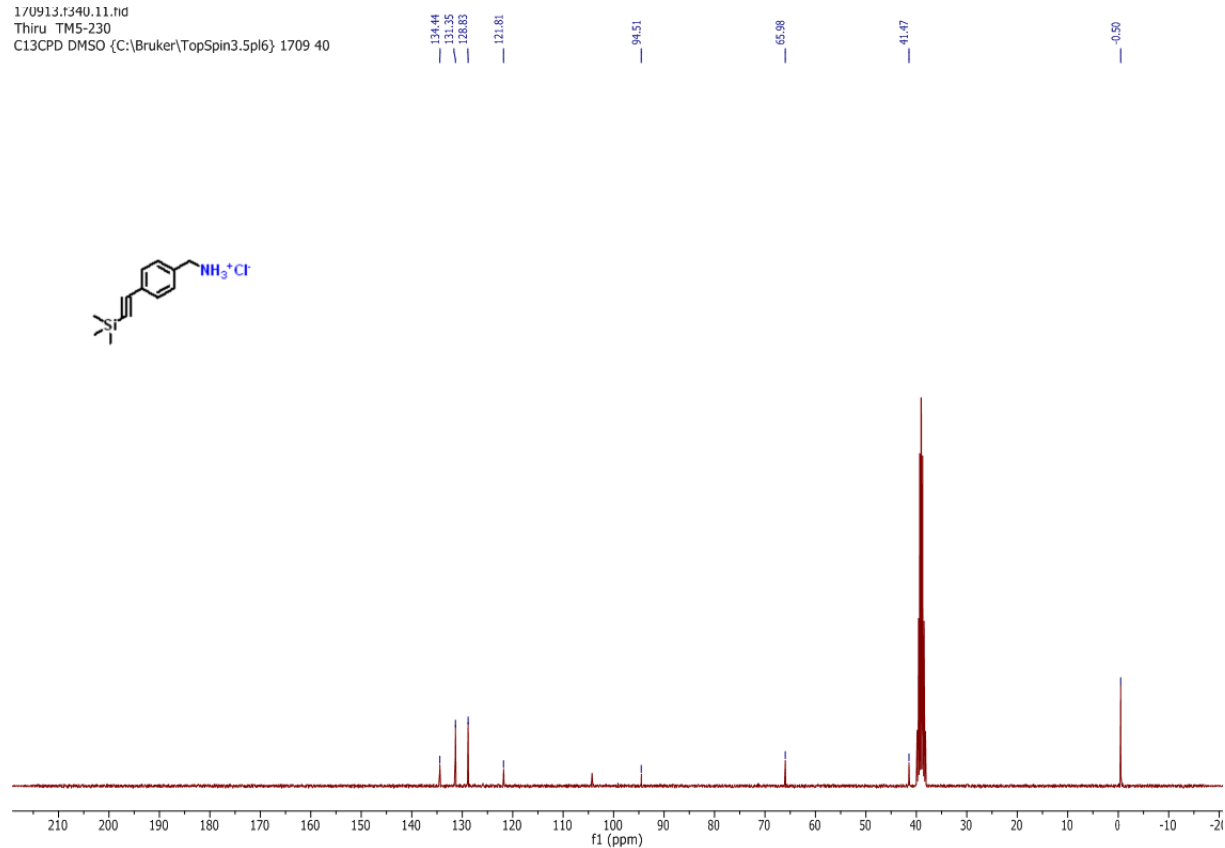
Supplementary Figure 57. ¹³C NMR spectrum

170913.f340.10.fid
Thiru_TMS-230
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 40



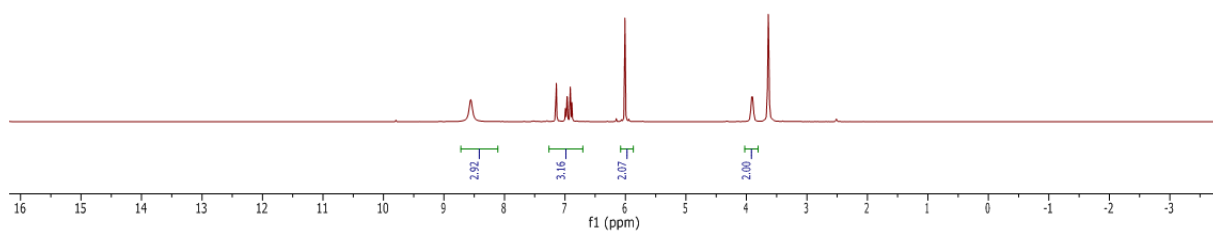
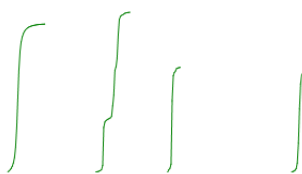
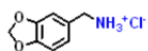
Supplementary Figure 58. ¹H NMR spectrum

170913.f340.11.fid
Thiru_TMS-230
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 40



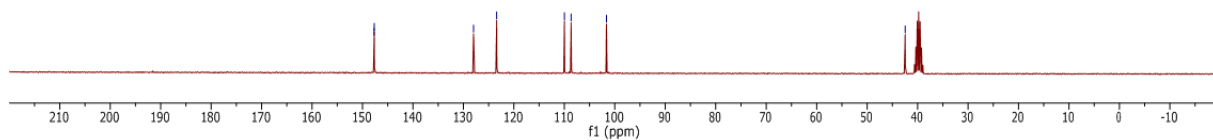
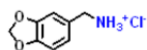
Supplementary Figure 59. ¹³C NMR spectrum

1/0922.f334.10.fid
Thiru/ TM5-336
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 34



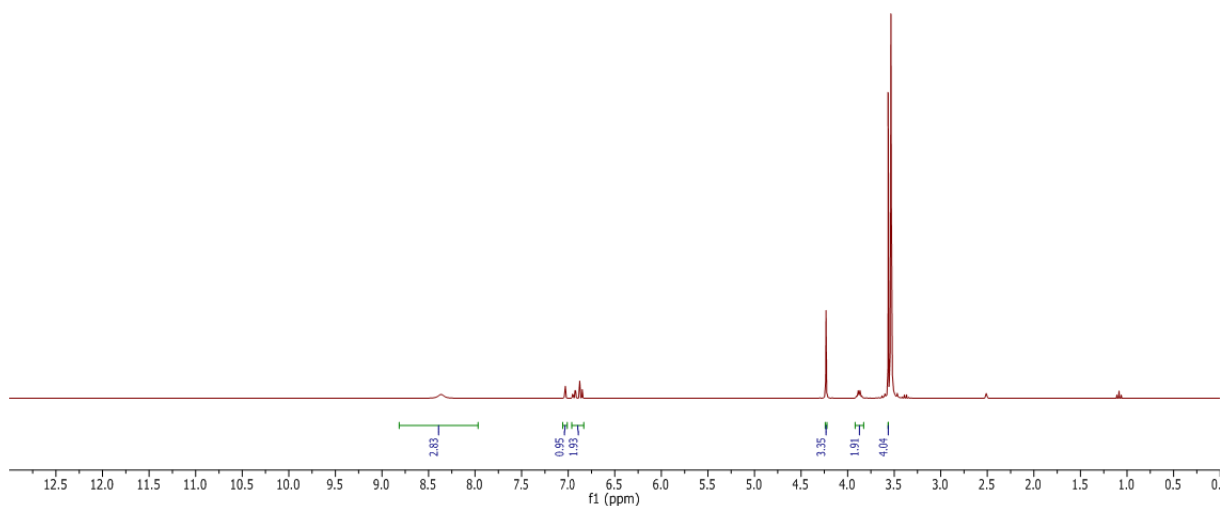
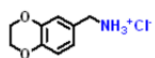
Supplementary Figure 60. ¹H NMR spectrum

1/0922.f334.11.fid
Thiru/ TM5-336
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 34



Supplementary Figure 61. ¹³C NMR spectrum

170913.1338.10.fid
Thiru TM5-183
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 38



Supplementary Figure 62. ^1H NMR spectrum

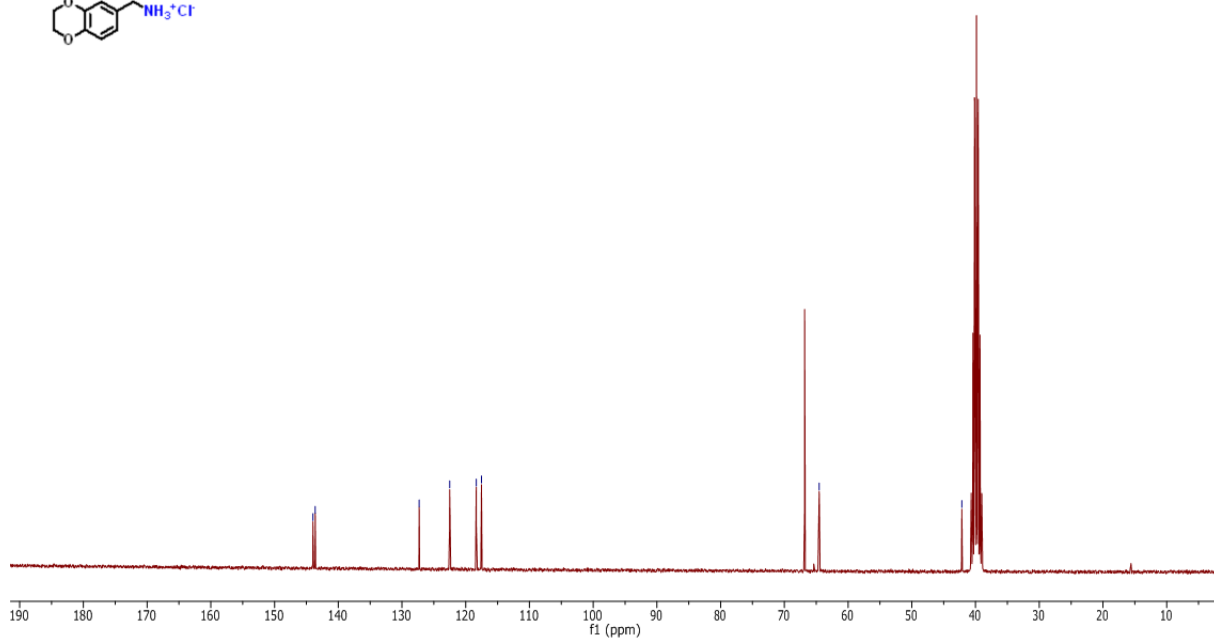
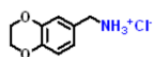
170913.1338.11.fid
Thiru TM5-183
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 38

143.98
143.62

127.30
123.63
118.34
117.53

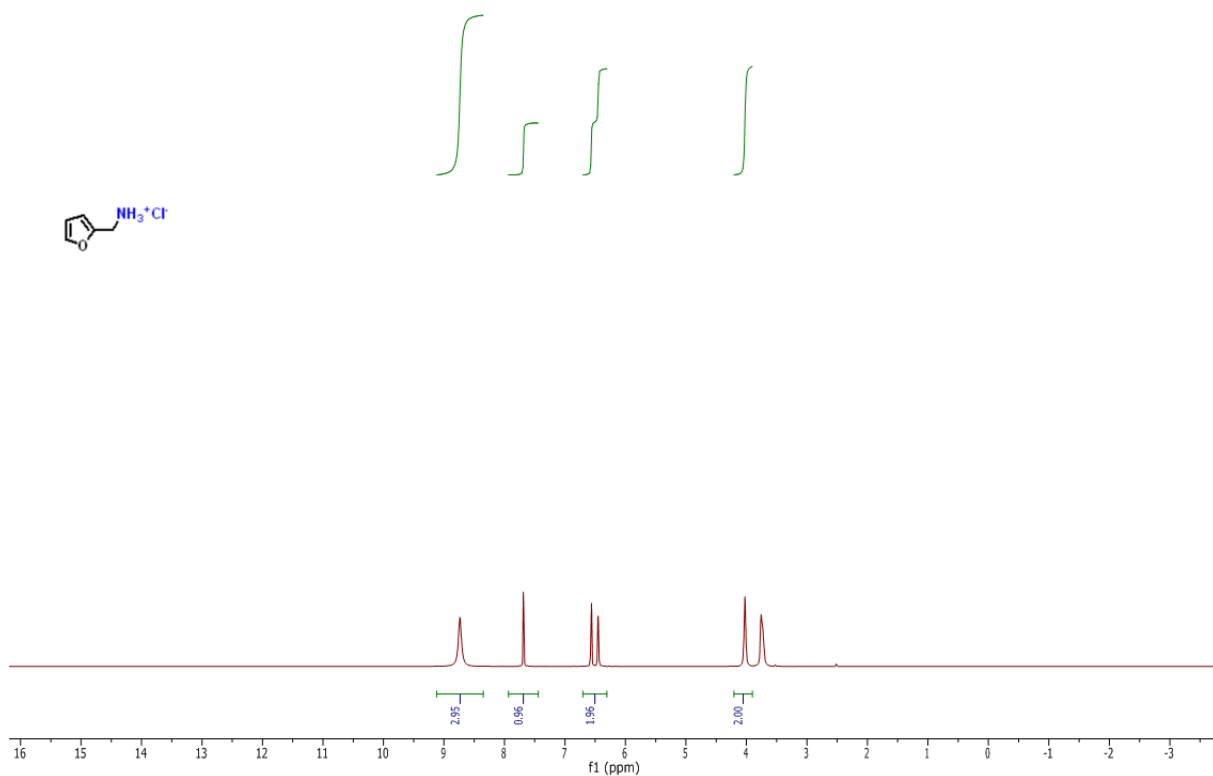
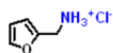
64.53

42.15



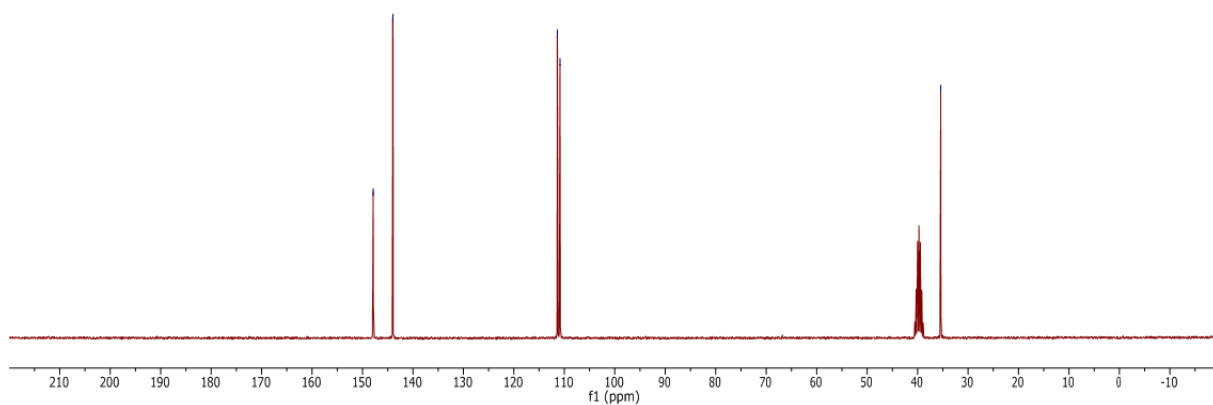
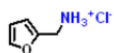
Supplementary Figure 63. ^{13}C NMR spectrum

1/0922.f342.10.fid
Thiru/ TM5-353
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 42



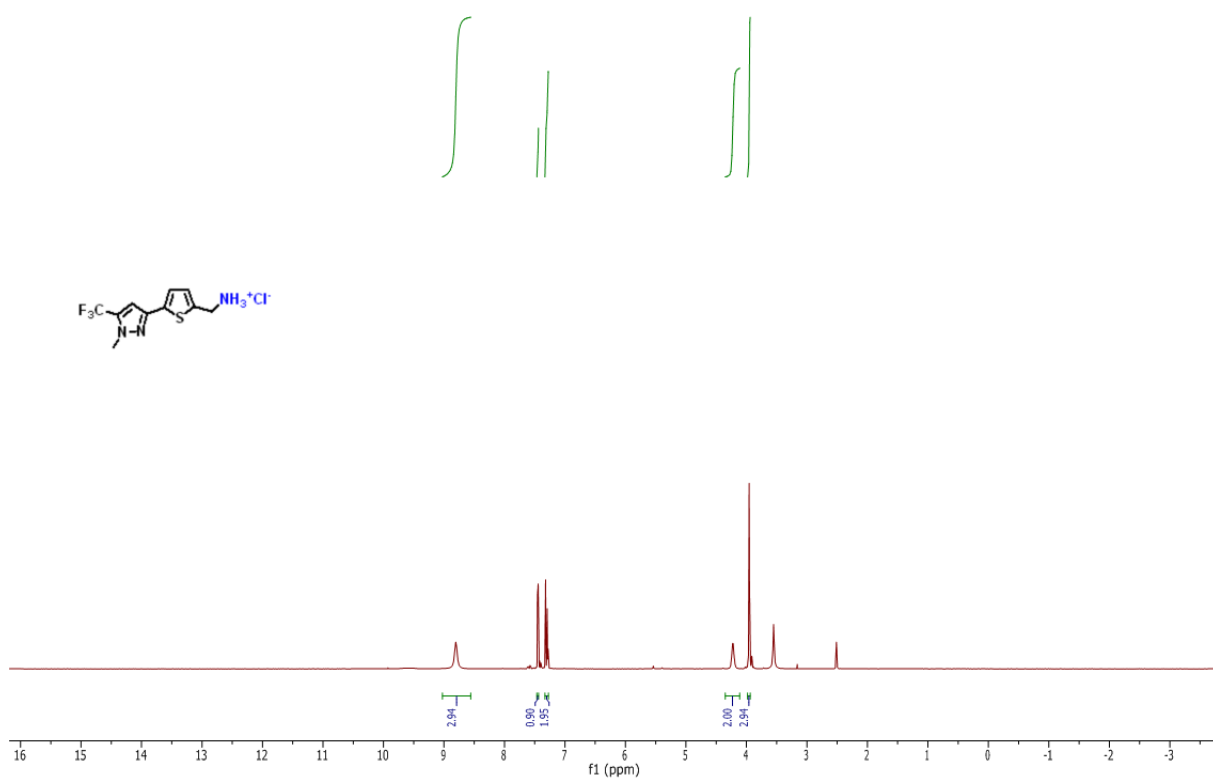
Supplementary Figure 64. ¹H NMR spectrum

1/0922.f342.11.fid
Thiru/ TM5-353
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 42



Supplementary Figure 65. ¹³C NMR spectrum

171004.f323.10.fid
Thiru TMS-196
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 23



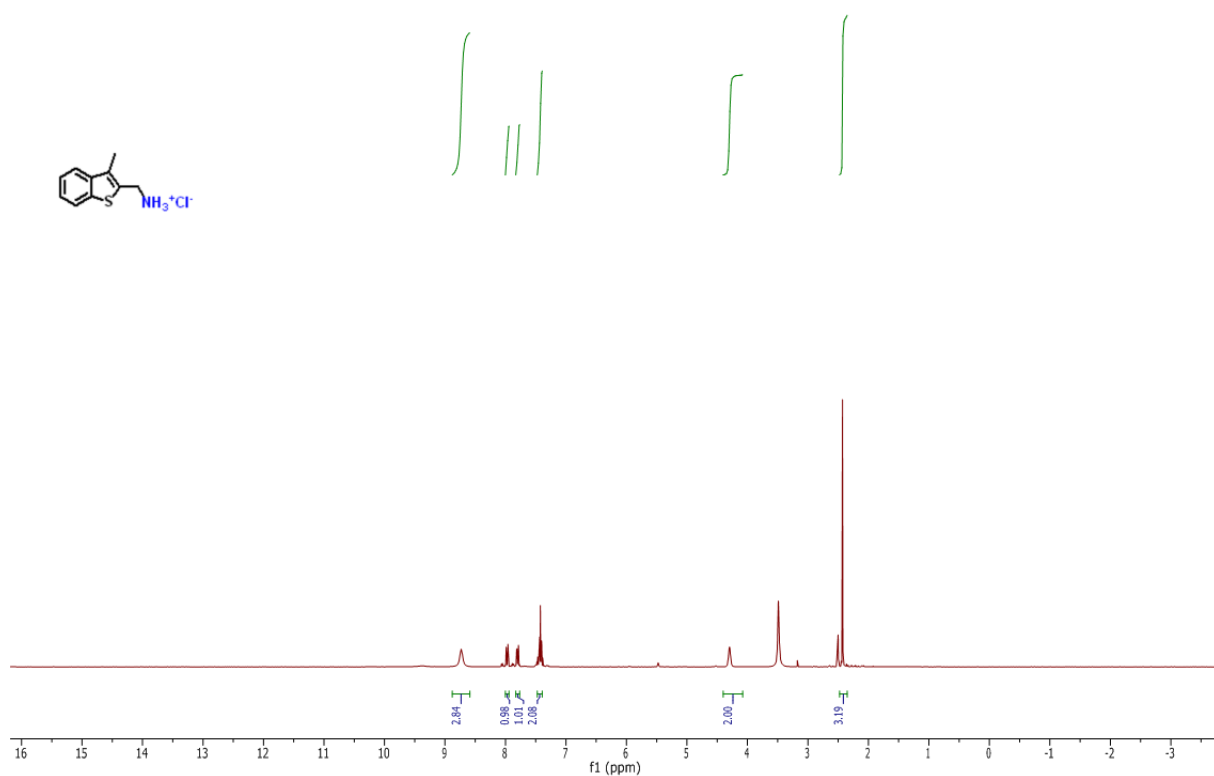
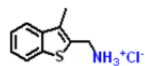
Supplementary Figure 66. ^1H NMR spectrum

171004.f323.11.fid
Thiru TMS-196
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 23



Supplementary Figure 67. ^{13}C NMR spectrum

1/1004.f322.10.fid
Thiru TM5-191
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 22

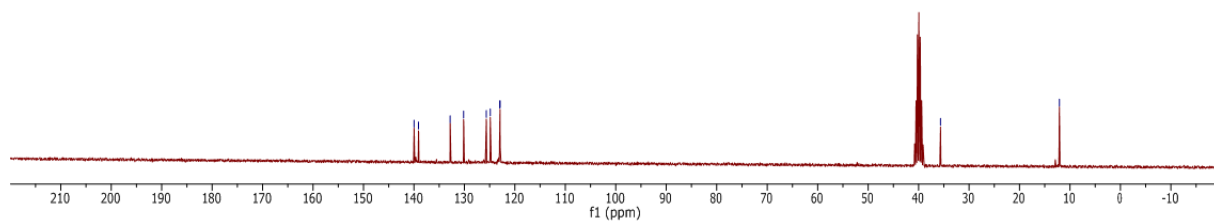
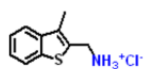


1/1004.f322.11.fid
Thiru TM5-191
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 22

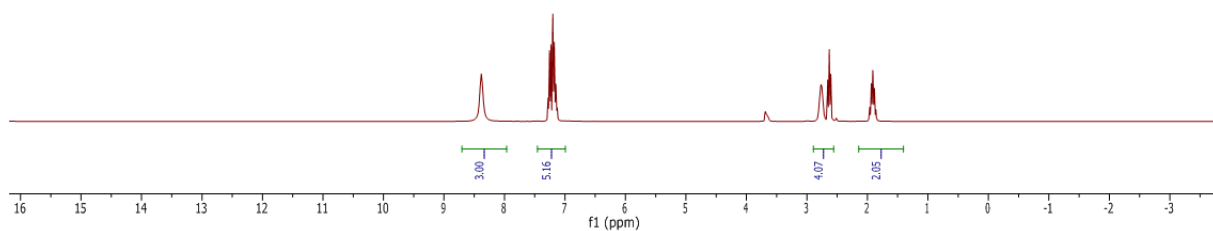
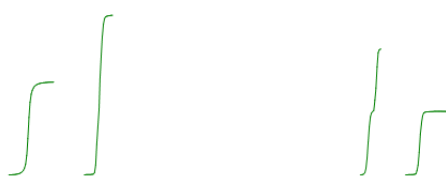
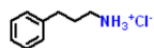
138.57
136.09
132.62
130.15
128.72
124.87
122.99
122.94

35.65

12.10



170922.f346.10.fid
Thiru/ TM5-195
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 46



Supplementary Figure 70. ¹H NMR spectrum

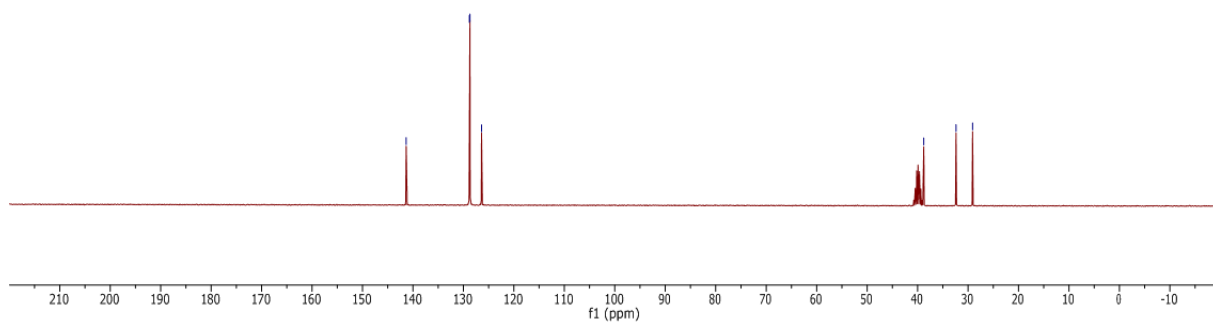
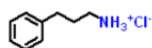
170922.f346.11.fid
Thiru/ TM5-195
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 46

141.35

128.82
128.71
126.41

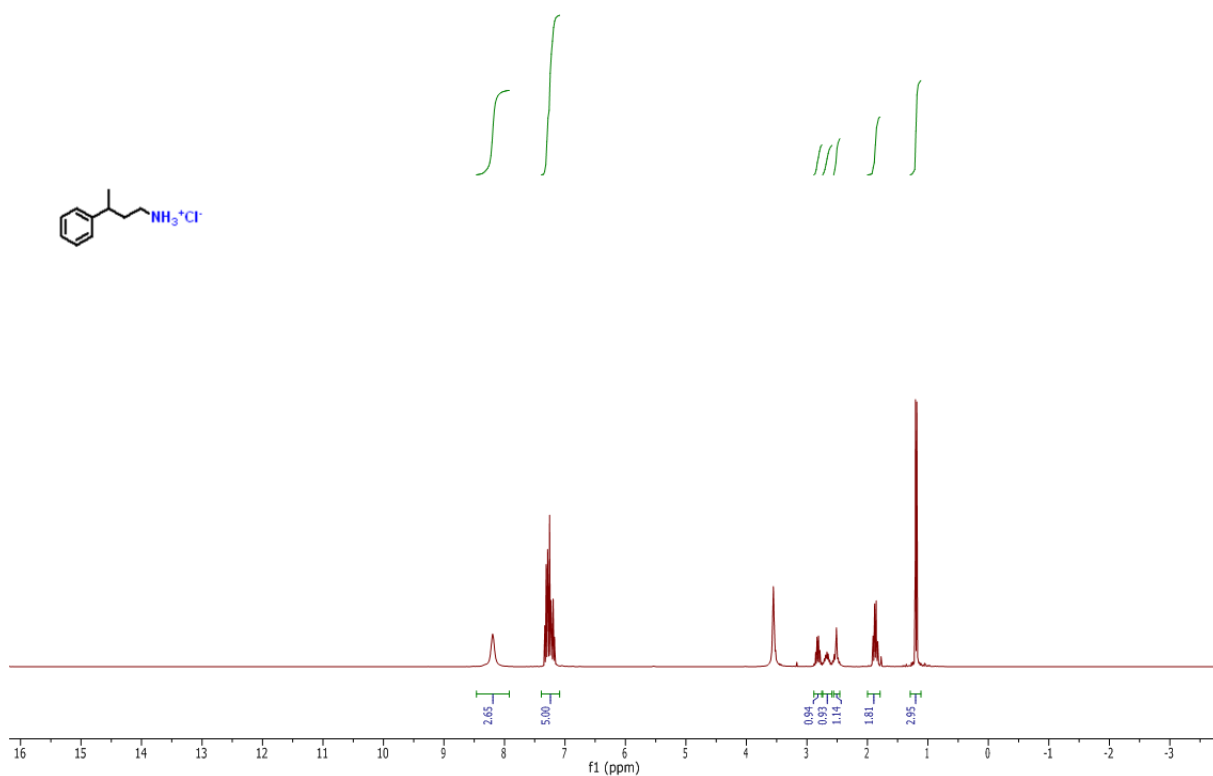
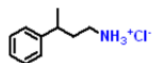
38.79

32.38
29.10



Supplementary Figure 71. ¹³C NMR spectrum

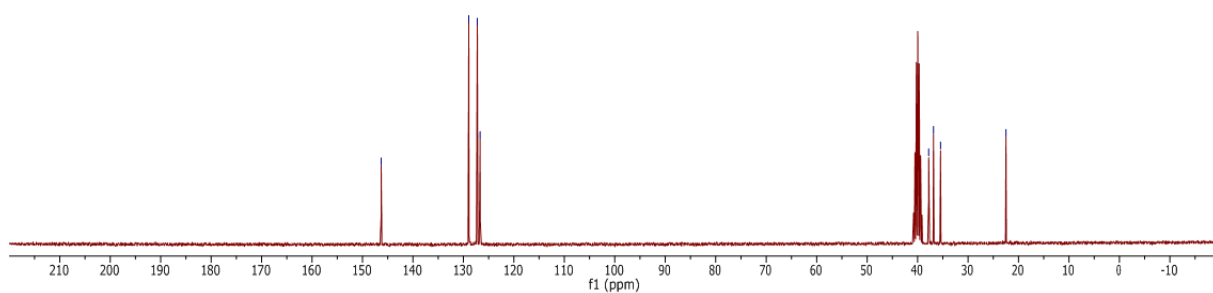
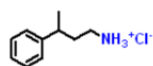
1/1004.f318.10.fid
Thiru TM5-211
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 18



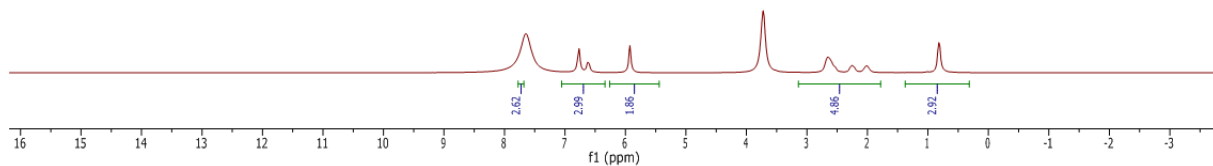
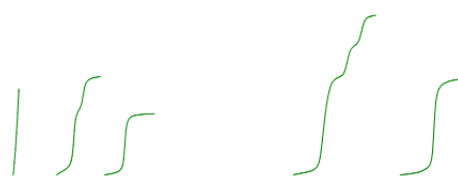
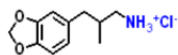
Supplementary Figure 72. ¹H NMR spectrum

1/1004.f318.11.fid
Thiru TM5-211
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 18

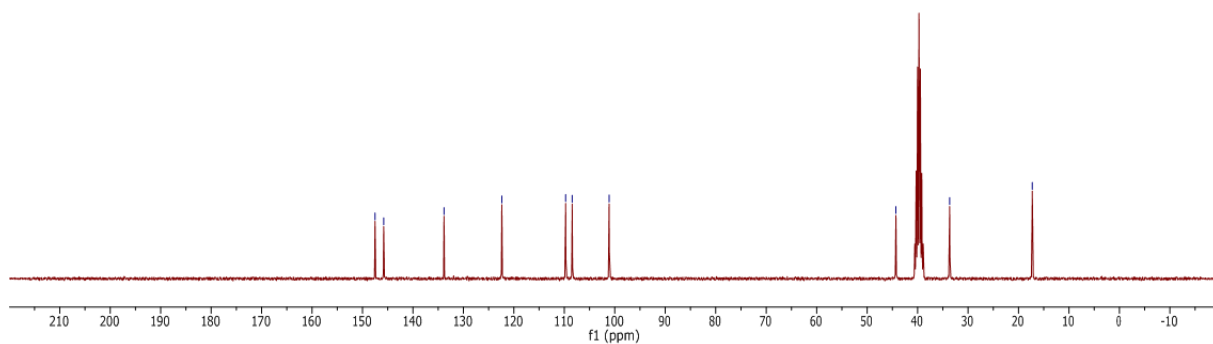
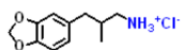
146.30
128.94
127.25
126.69
37.79
36.85
35.45
22.49



Supplementary Figure 73. ¹³C NMR spectrum

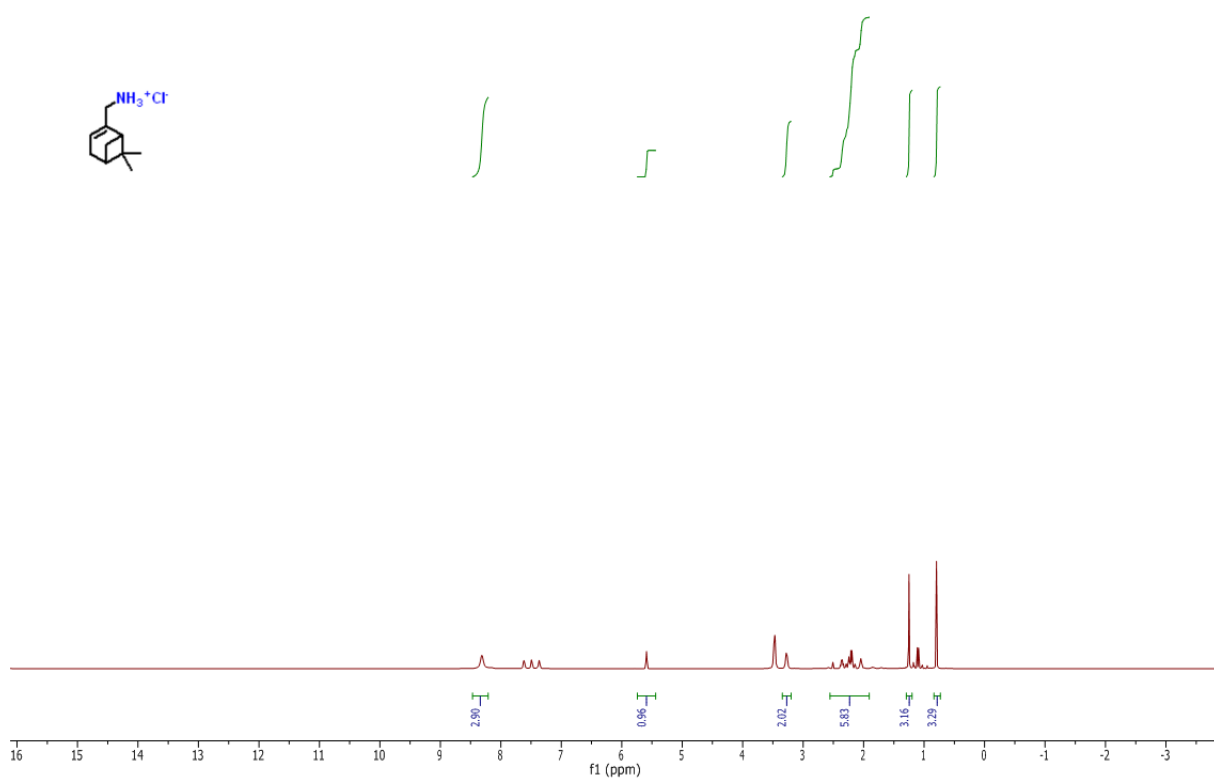


Supplementary Figure 74. ¹H NMR spectrum



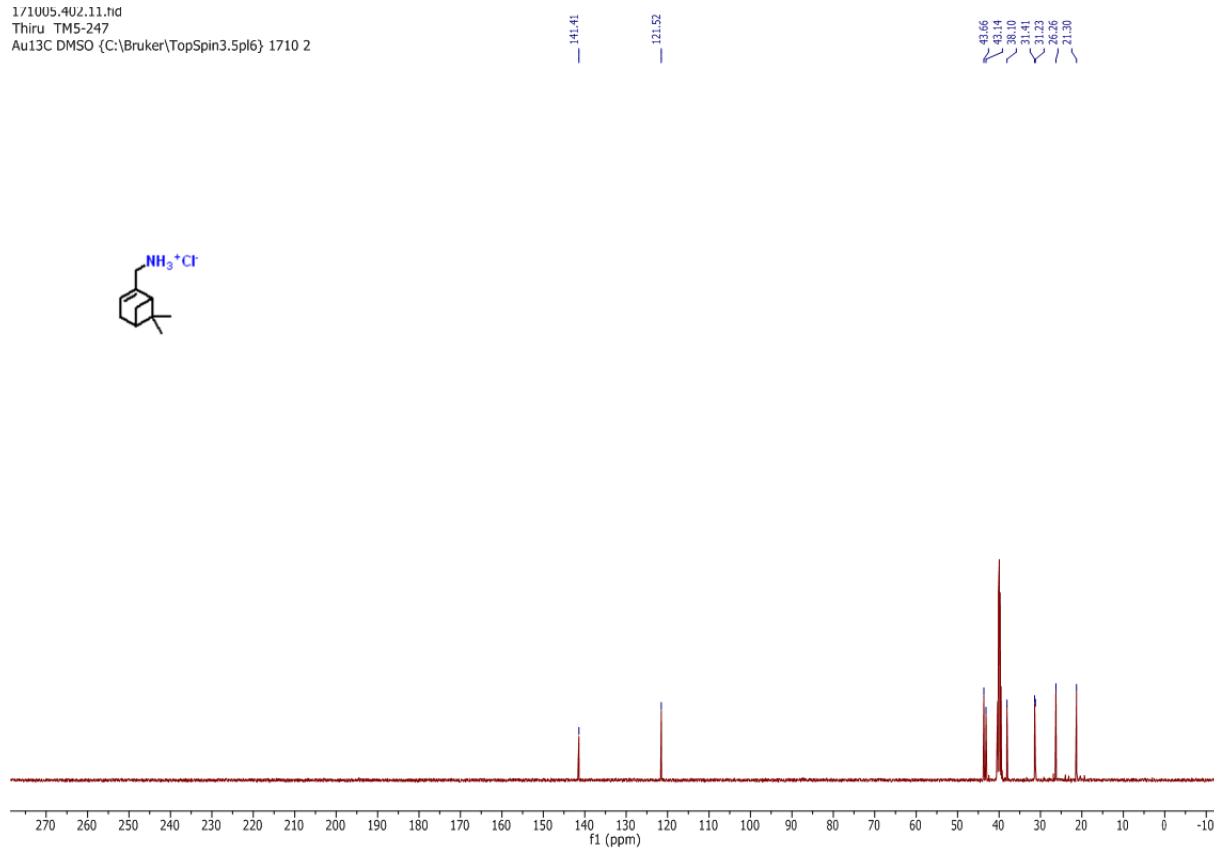
Supplementary Figure 75. ¹³C NMR spectrum

1/1005.402.10.nd
Thiru TMS-247
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1710 2



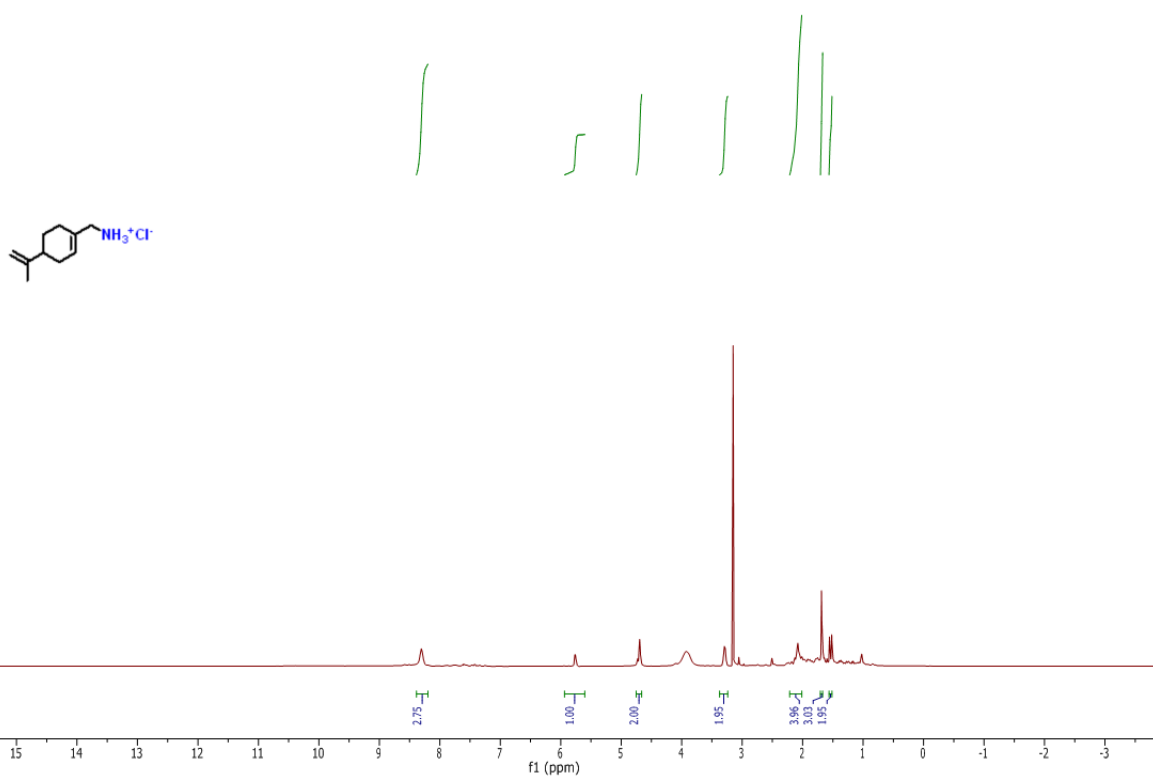
Supplementary Figure 76. ¹H NMR spectrum

1/1005.402.11.nd
Thiru TMS-247
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1710 2



Supplementary Figure 77. ¹³C NMR spectrum

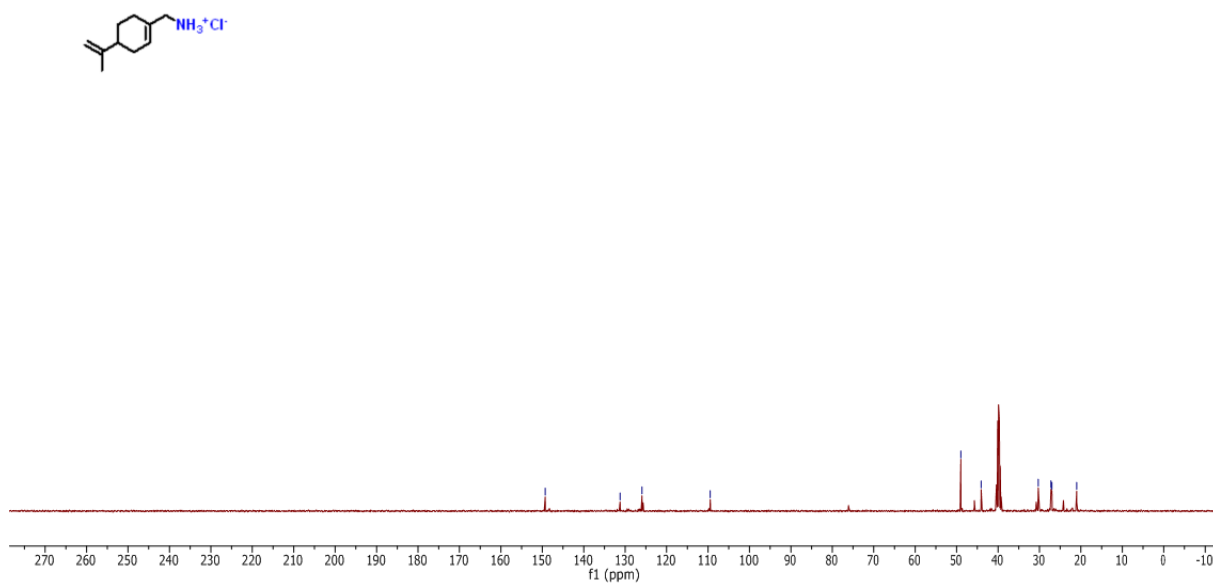
1/1005.407.10.nd
Thiru TMS-327
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1710 7



Supplementary Figure 78. ¹H NMR spectrum

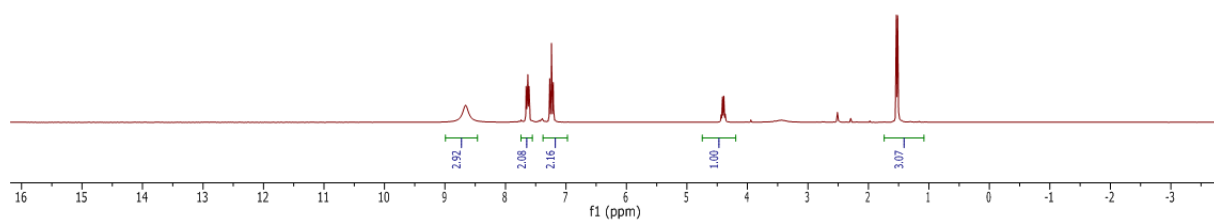
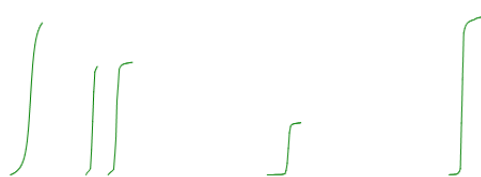
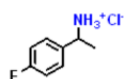
1/1005.407.11.nd
Thiru TMS-327
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1710 7

149.31
131.23
125.94
109.47
48.98
44.07
30.79
27.22
27.01
21.02



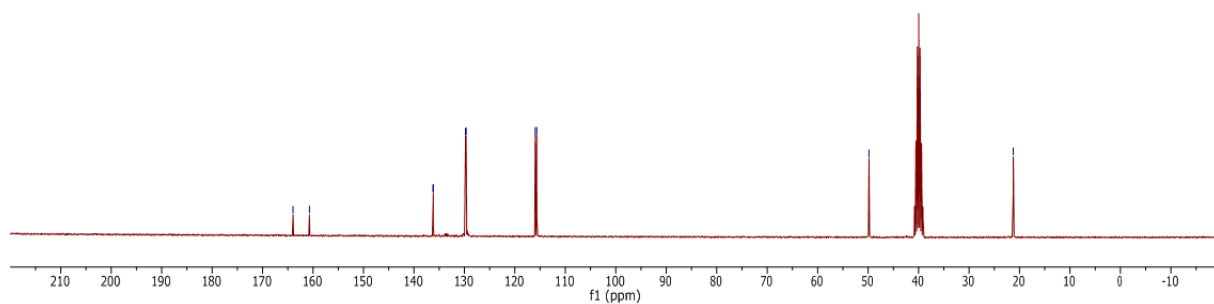
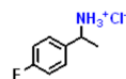
Supplementary Figure 79. ¹³C NMR spectrum

170925.f340.10.fid
Thiru TMS-283
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 40



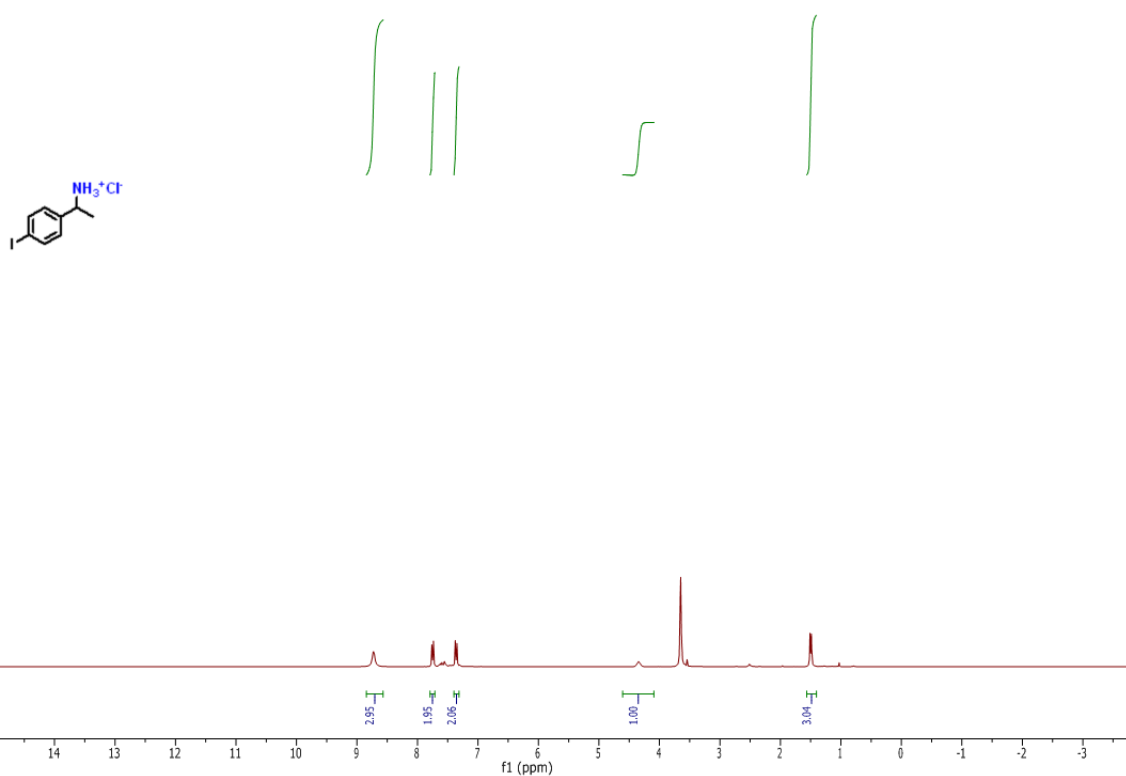
Supplementary Figure 80. ^1H NMR spectrum

170925.f340.11.fid
Thiru TMS-283
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 40



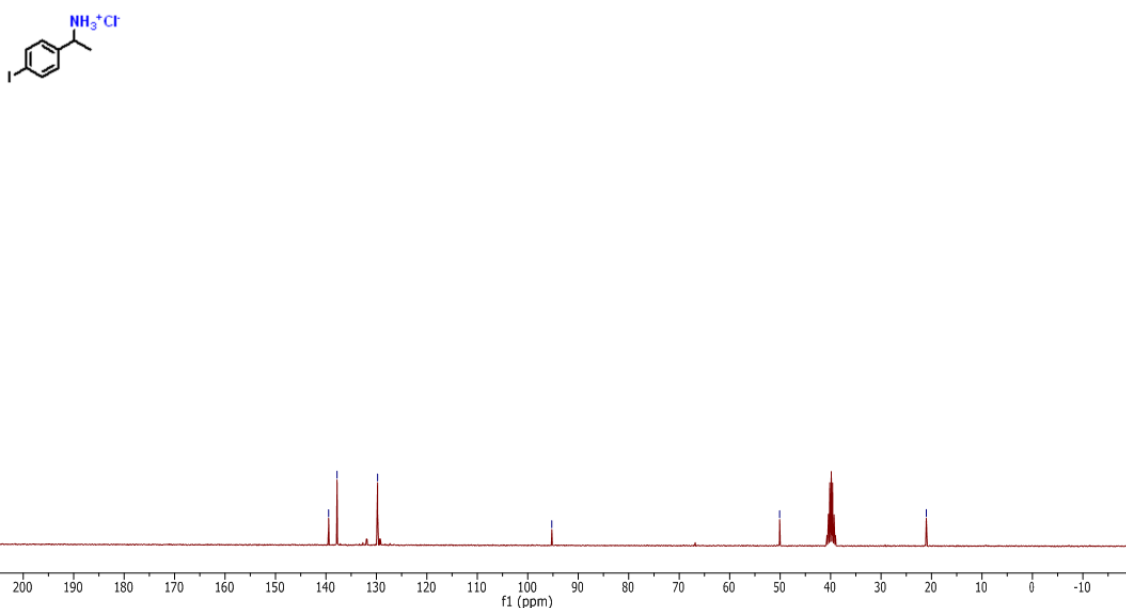
Supplementary Figure 81. ^{13}C NMR spectrum

170922.f337.110.tif
Thiru/ TM5-337
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 37

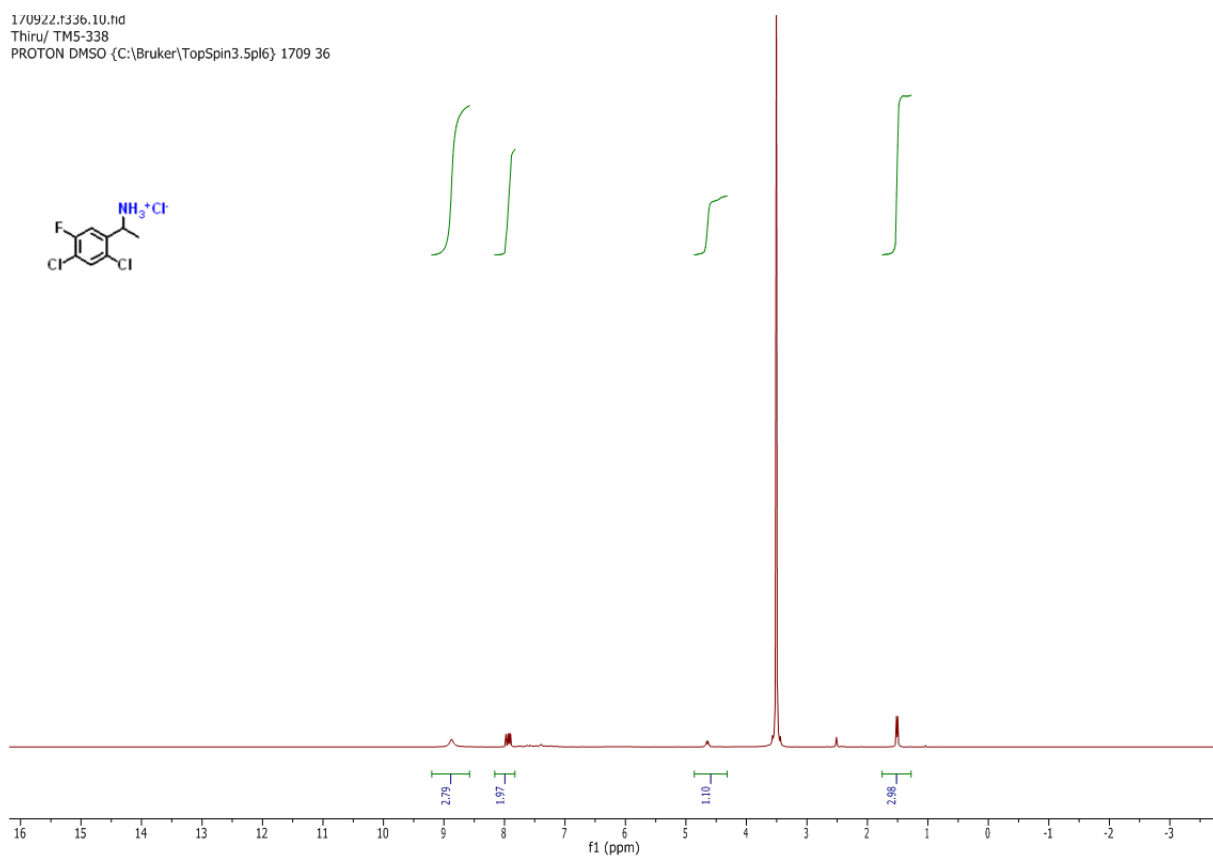
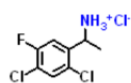


170922.f337.111.tif
Thiru/ TM5-337
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 37

139.47
137.80
128.78
95.24
50.09
21.03

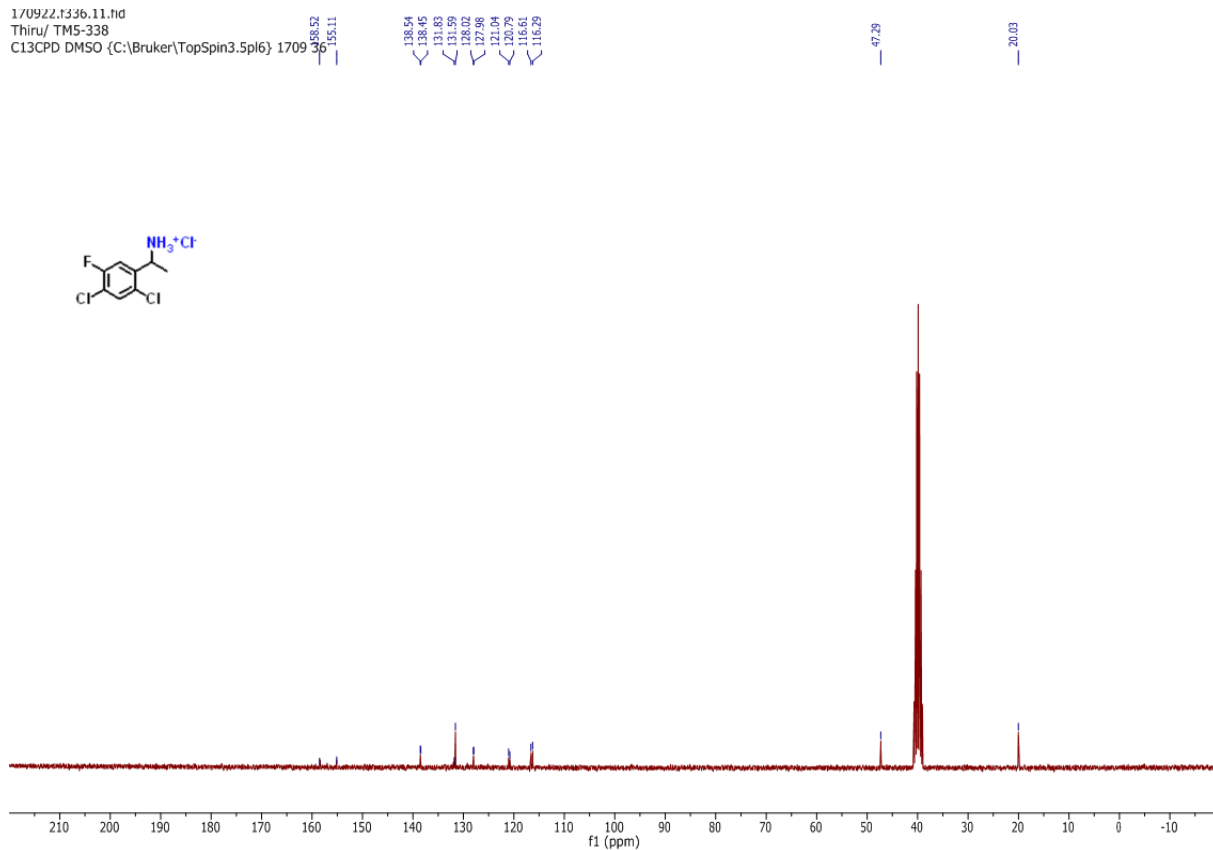
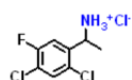


1/0922.f336.10.fid
Thiru/ TM5-338
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 36

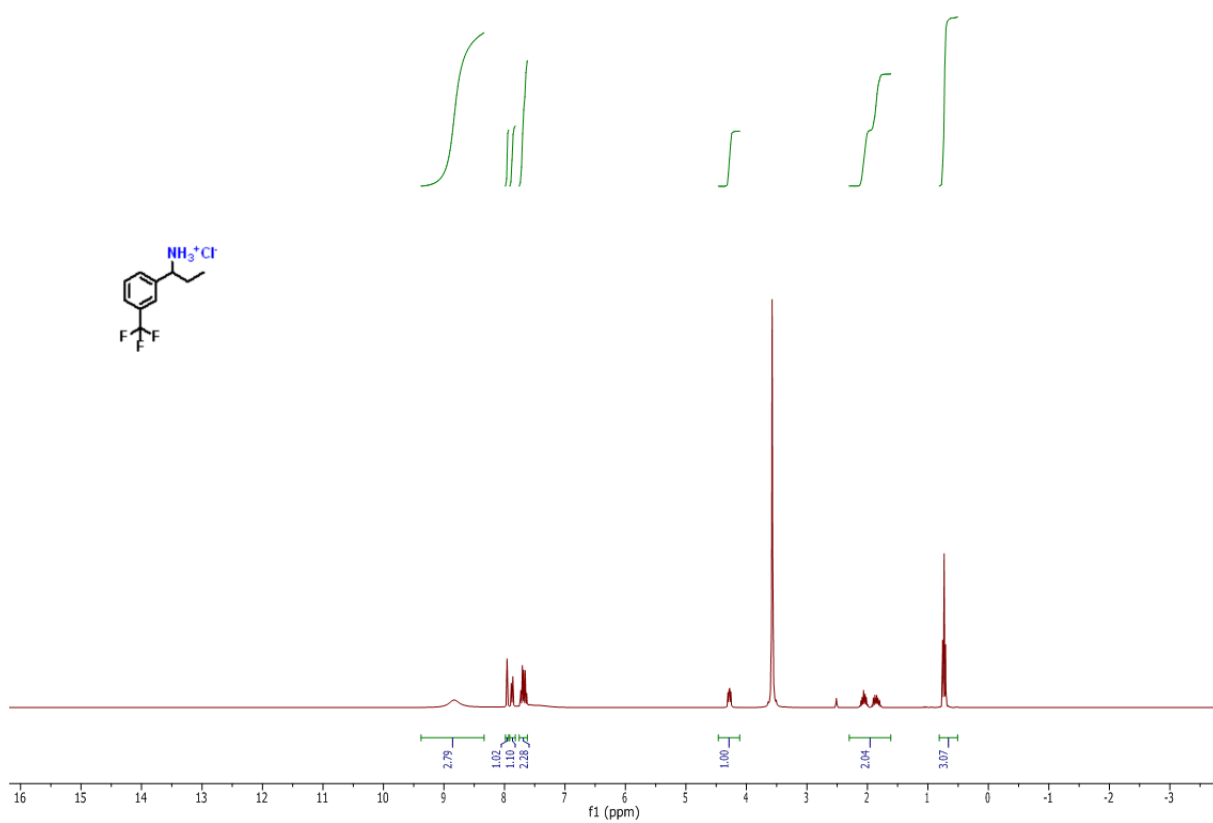


Supplementary Figure 84. ¹H NMR spectrum

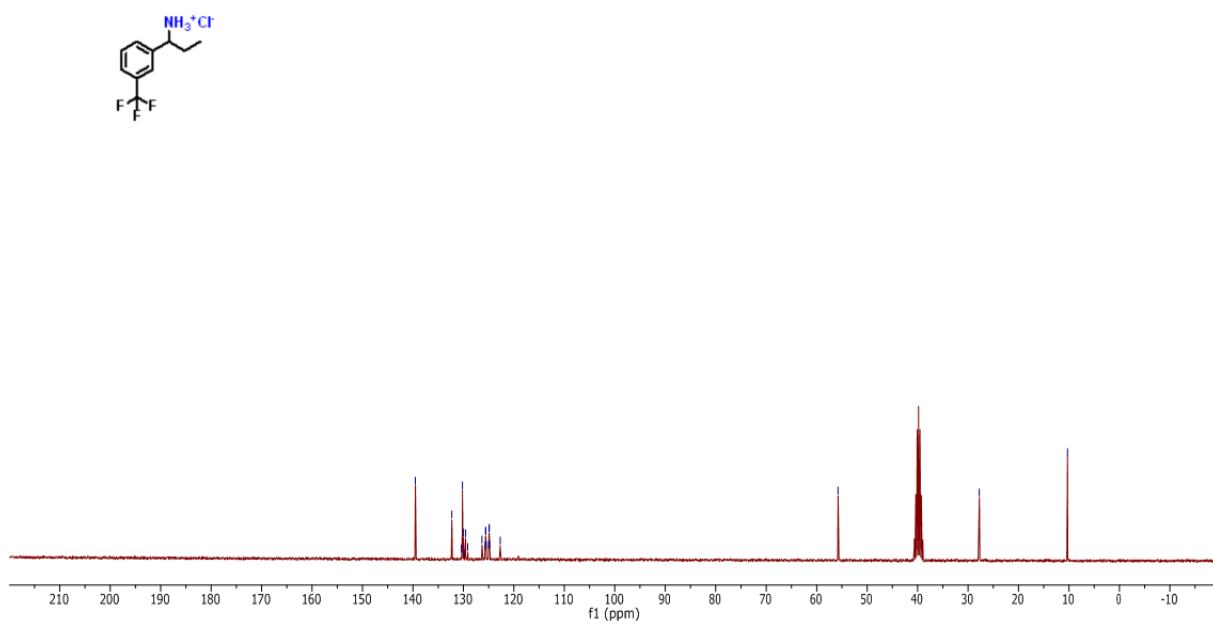
1/0922.f336.11.fid
Thiru/ TM5-338
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 36



Supplementary Figure 85. ¹³C NMR spectrum

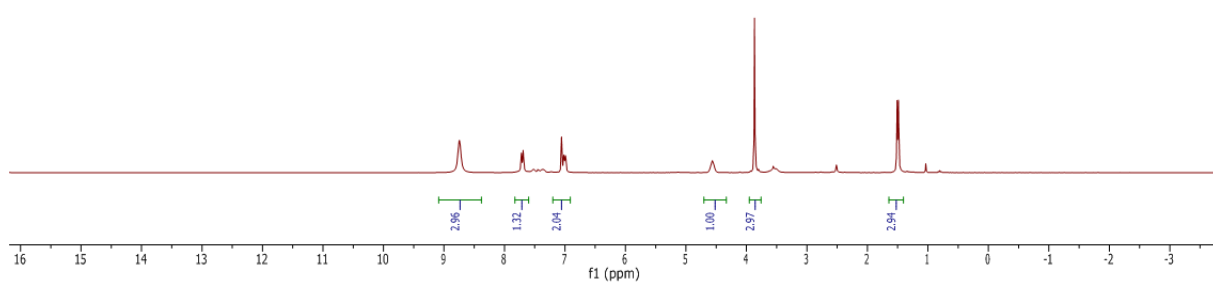
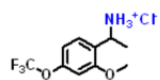


Supplementary Figure 86. ^1H NMR spectrum



Supplementary Figure 87. ^{13}C NMR spectrum

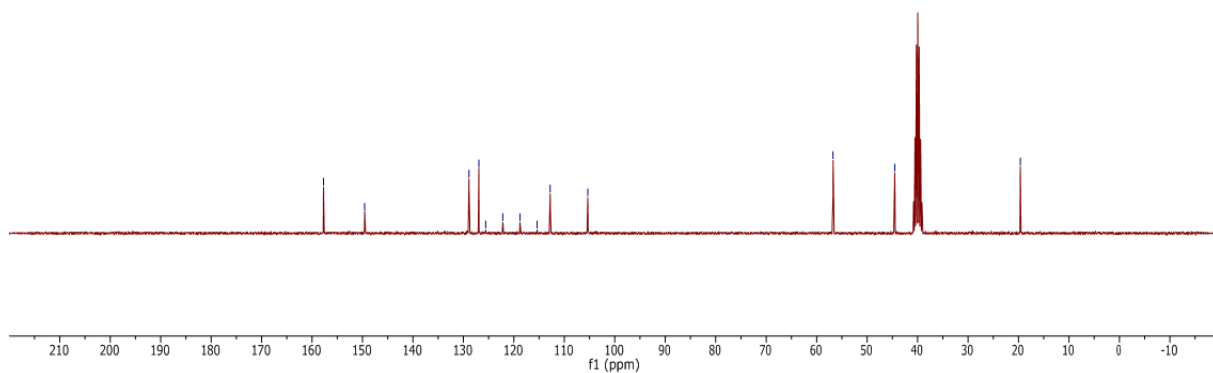
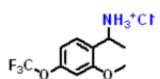
1/0922.f332.10.fid
Thiru/ TM5-362
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 32



Supplementary Figure 88. ¹H NMR spectrum

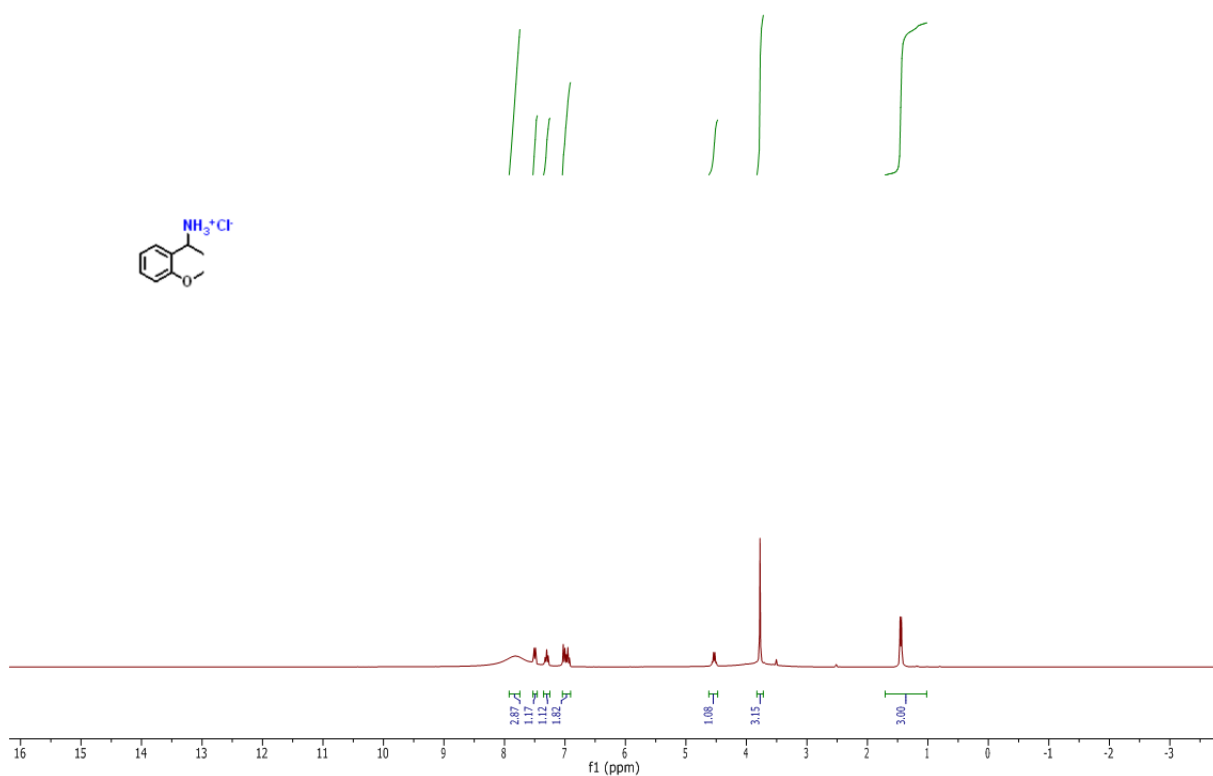
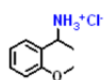
1/0922.f332.11.fid
Thiru/ TM5-362
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 32

157.73 149.58 126.89 126.84 125.59 122.19 118.79 115.40 112.81 105.36 56.75 44.52 19.63



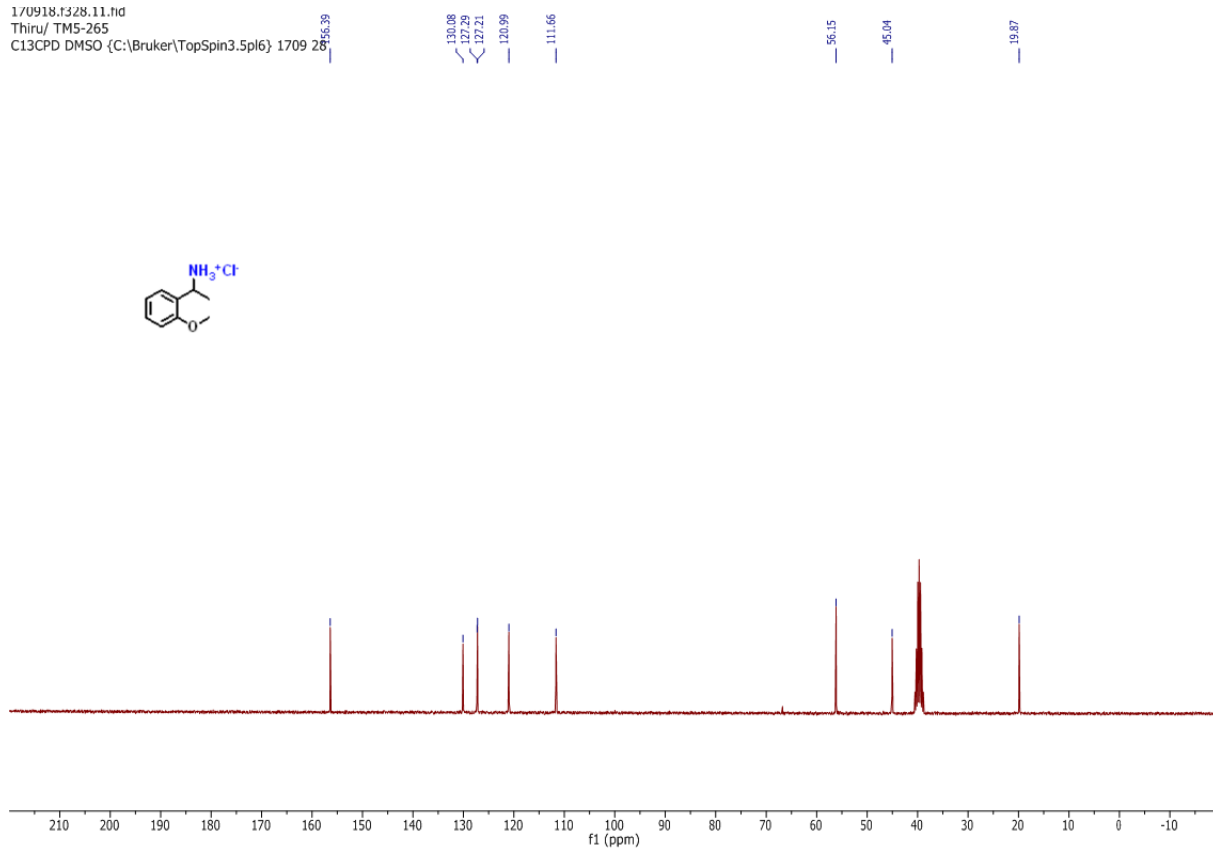
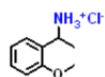
Supplementary Figure 90. ¹³C NMR spectrum

1/0918.f328.10.fid
Thiru/ TM5-265
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 28



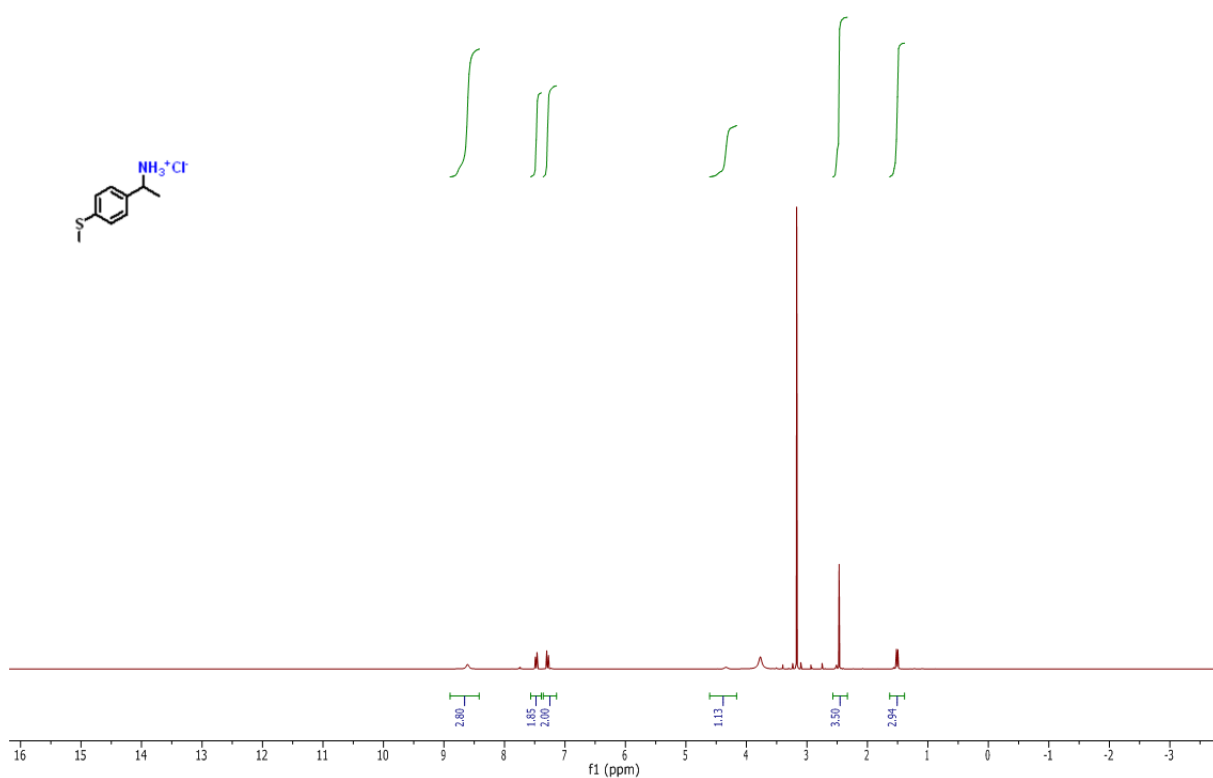
Supplementary Figure 91. ^1H NMR spectrum

1/0918.f328.11.fid
Thiru/ TM5-265
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 28



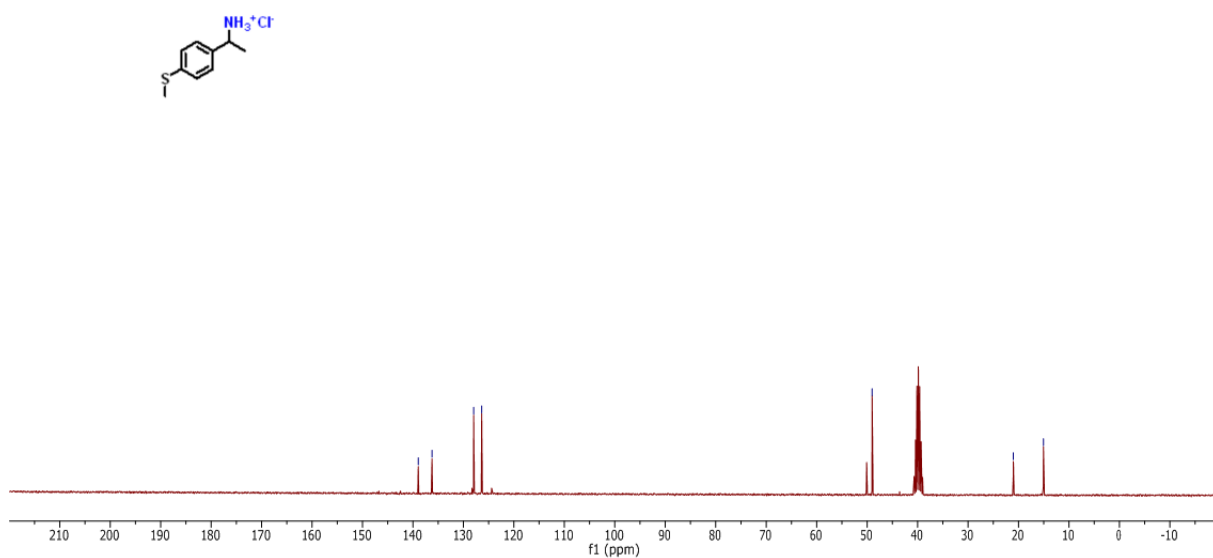
Supplementary Figure 92. ^{13}C NMR spectrum

1/1004.f325.10.fid
Thiru TM5-289
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 25



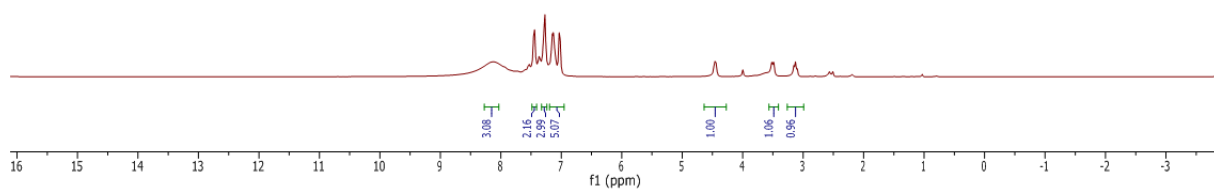
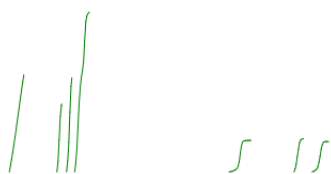
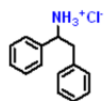
Supplementary Figure 93. ¹H NMR spectrum

1/1004.f325.11.fid
Thiru TM5-289
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 25



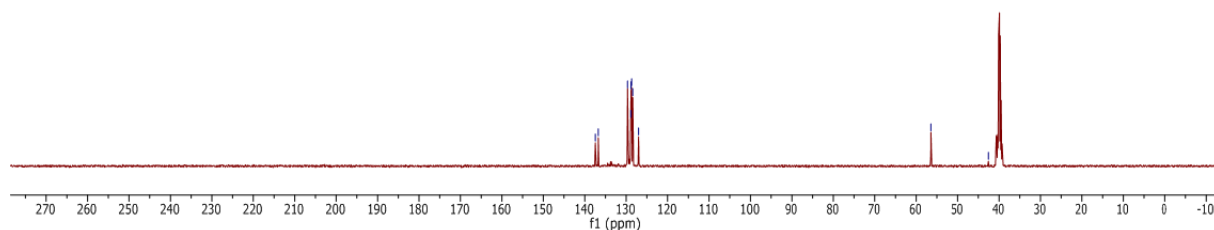
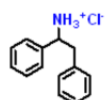
Supplementary Figure 94. ¹³C NMR spectrum

170928.443.10.nd
Thiru TMS-301
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 43



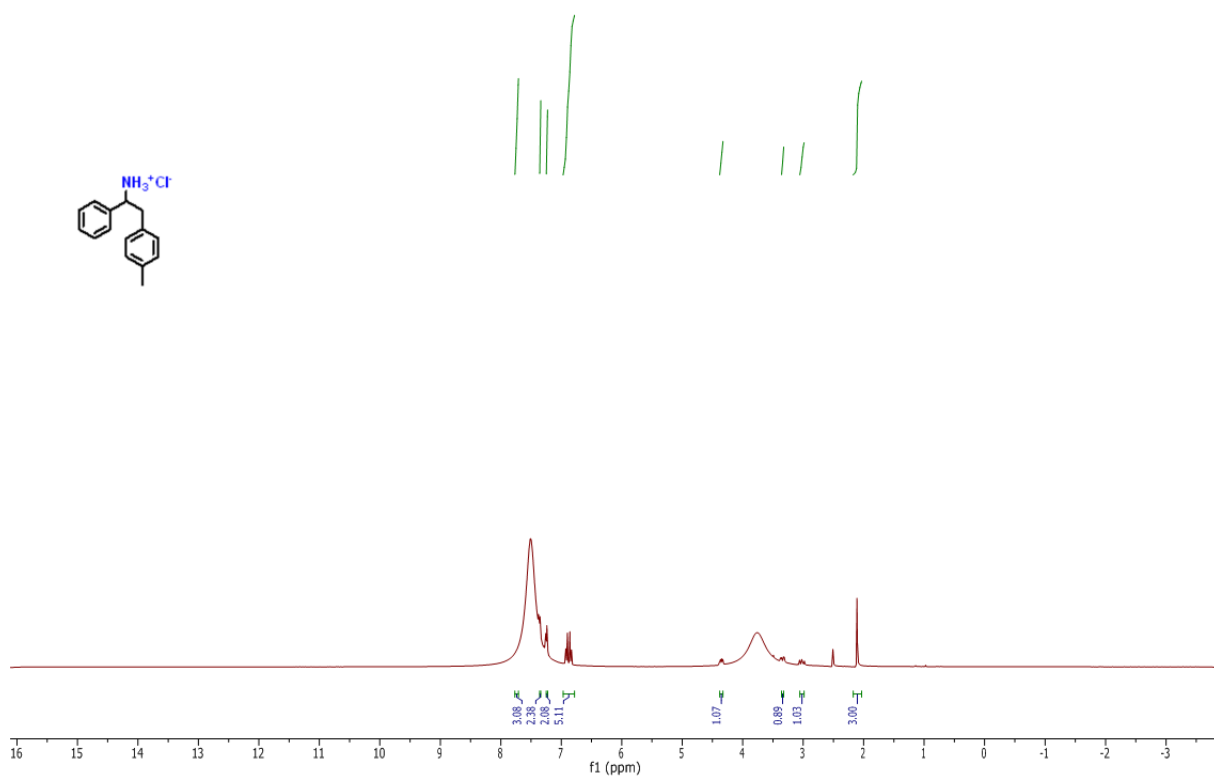
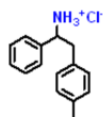
Supplementary Figure 95. ¹H NMR spectrum

170928.443.11.nd
Thiru TMS-301
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 43



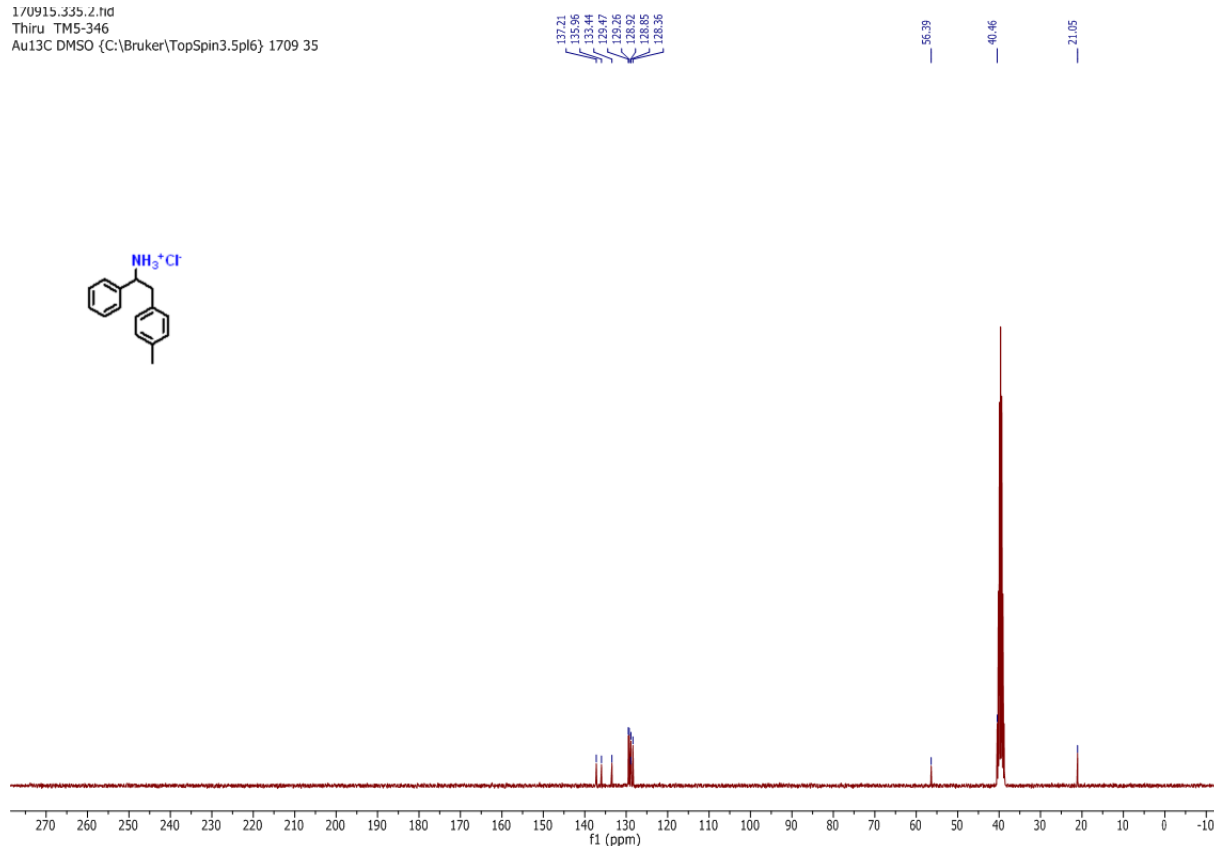
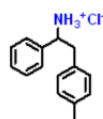
Supplementary Figure 96. ¹³C NMR spectrum

1/0915.335.1.fid
Thiru TM5-346
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 35



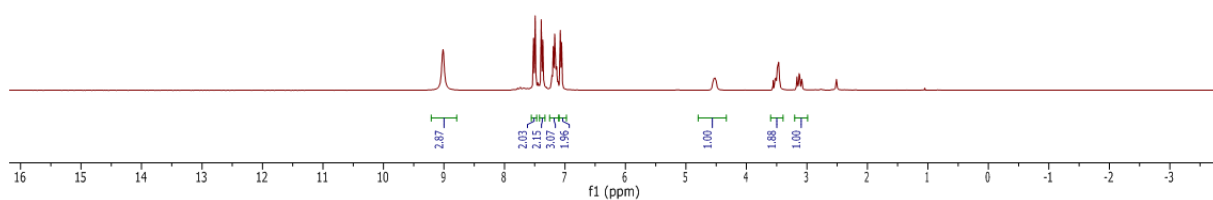
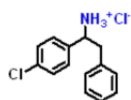
Supplementary Figure 97. ¹H NMR spectrum

1/0915.335.2.fid
Thiru TM5-346
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 35



Supplementary Figure 98. ¹³C NMR spectrum

1/0922.f333.10.fid
Thiru/ TMS-300
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 33

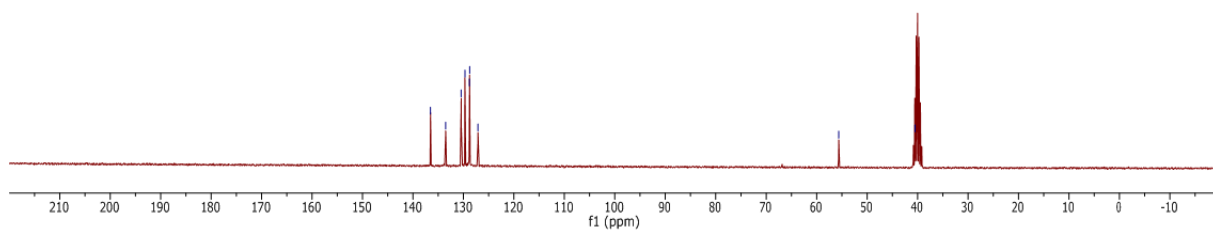
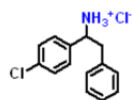


Supplementary Figure 99. ¹H NMR spectrum

1/0922.f333.11.fid
Thiru/ TMS-300
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 33

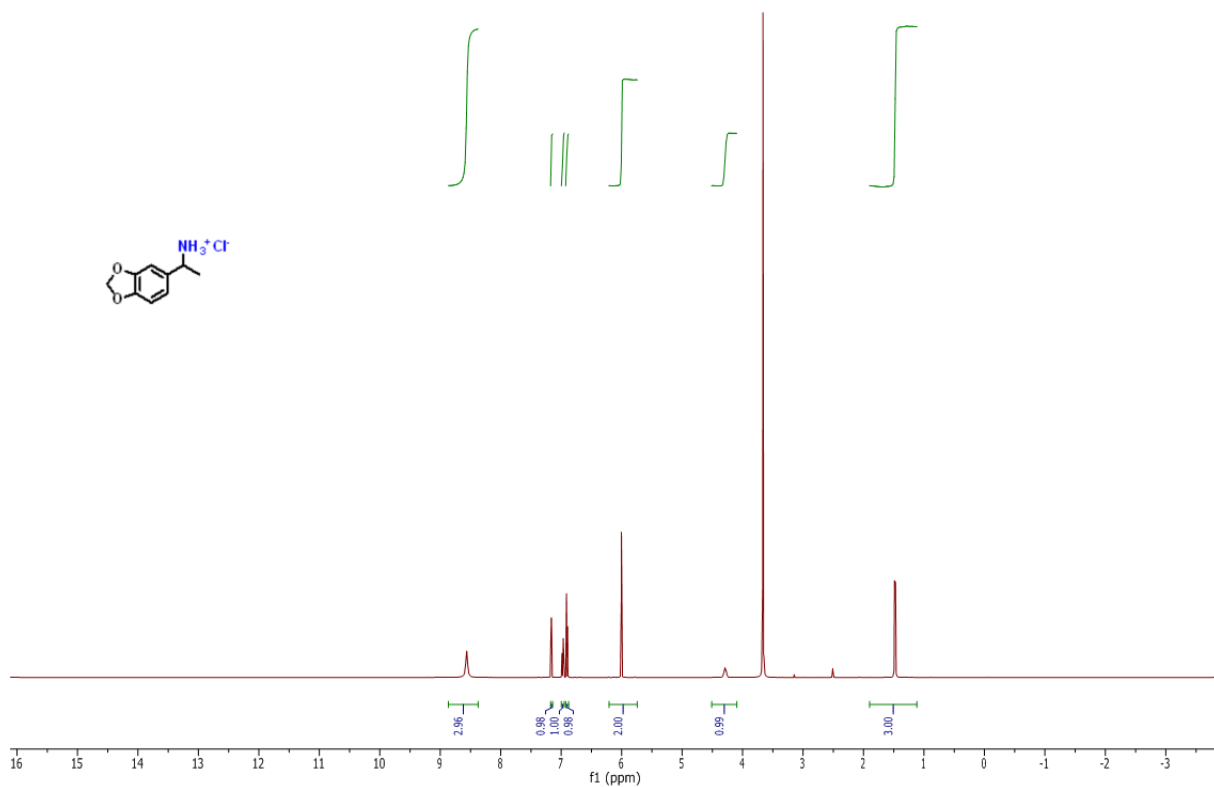
136.52
133.52
130.44
129.70
128.92
127.77
127.11

55.63
40.50



Supplementary Figure 100. ¹³C NMR spectrum

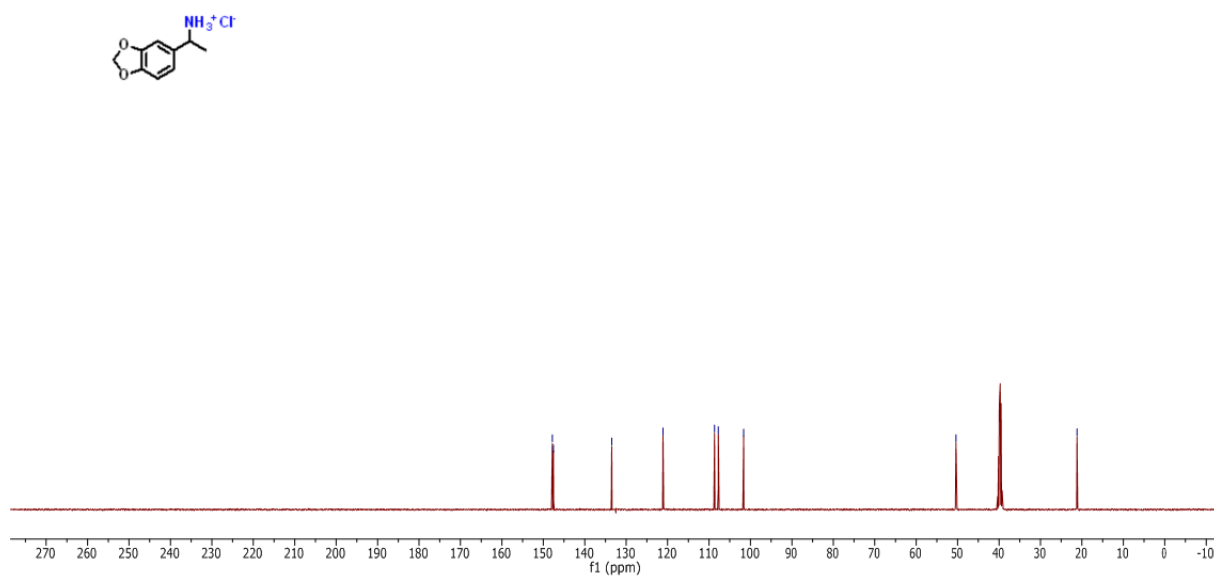
1/1005.404.10.nd
Thiru TM5-294
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1710 4



Supplementary Figure 101. ^1H NMR spectrum

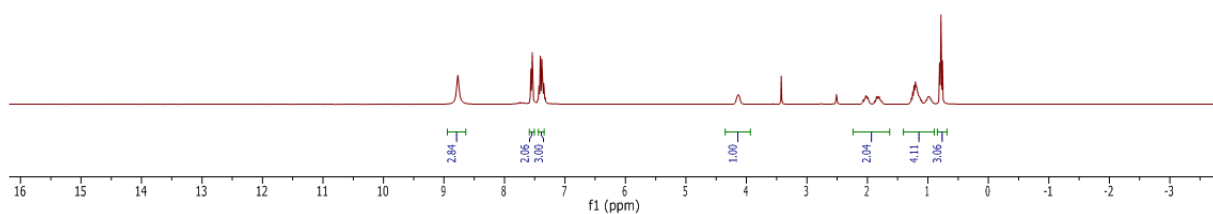
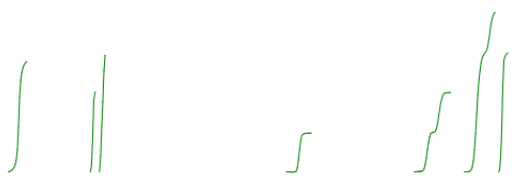
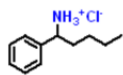
1/1005.404.11.nd
Thiru TM5-294
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1710 4

147.82
147.55
133.49
121.12
108.68
107.76
101.65
50.40
21.19



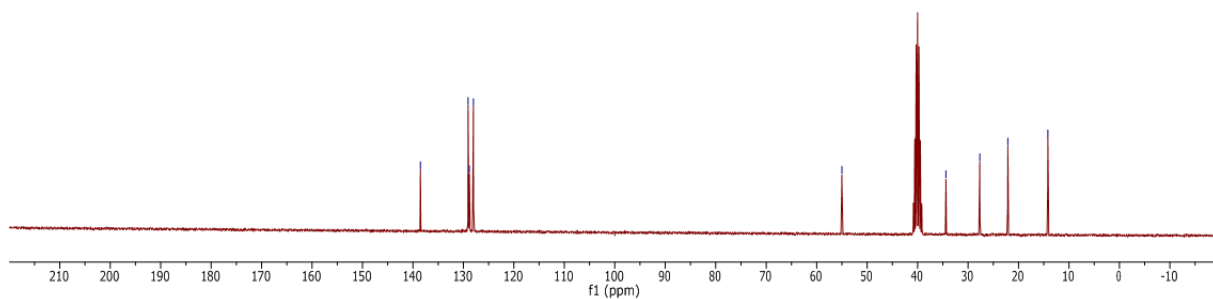
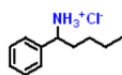
Supplementary Figure 102. ^{13}C NMR spectrum

170922.f339.10.fid
Thiru/ TM5-279
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 39



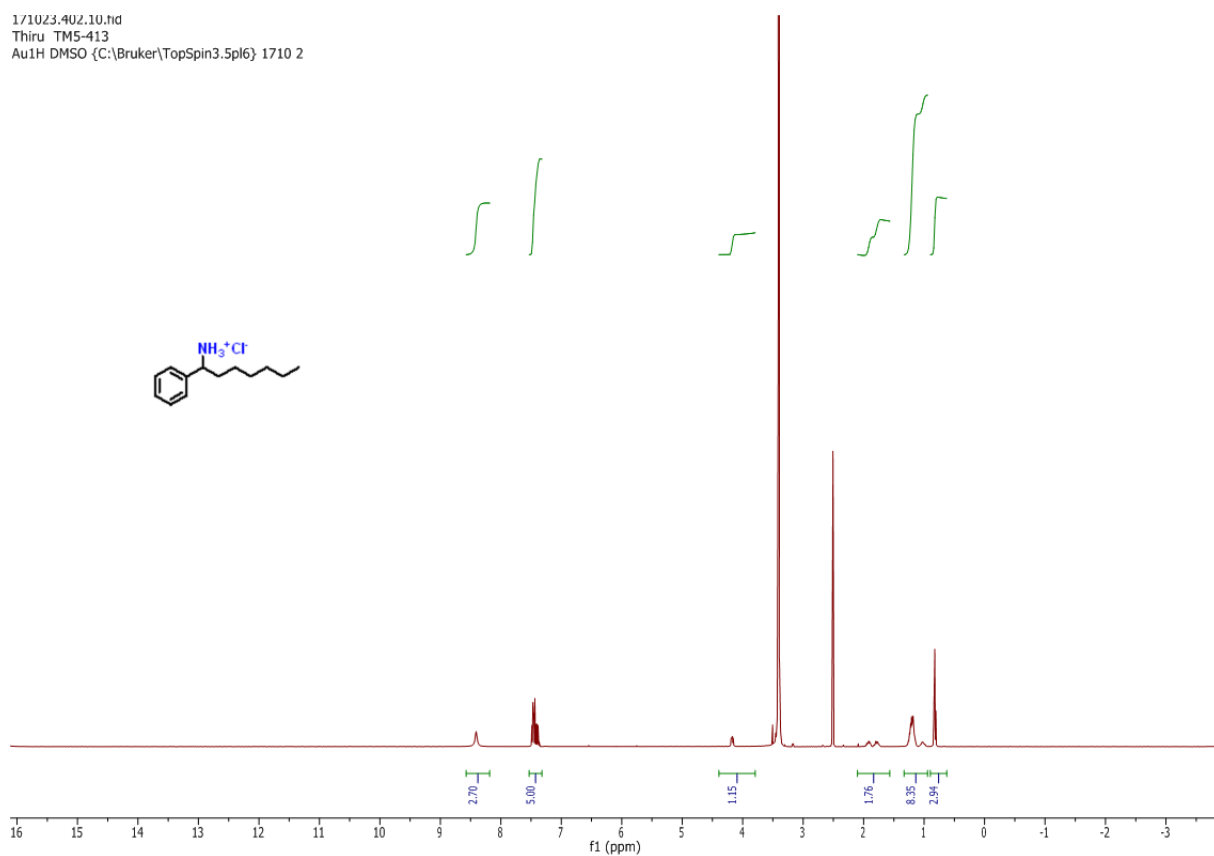
Supplementary Figure 103. ¹H NMR spectrum

170922.f339.11.fid
Thiru/ TM5-279
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 39



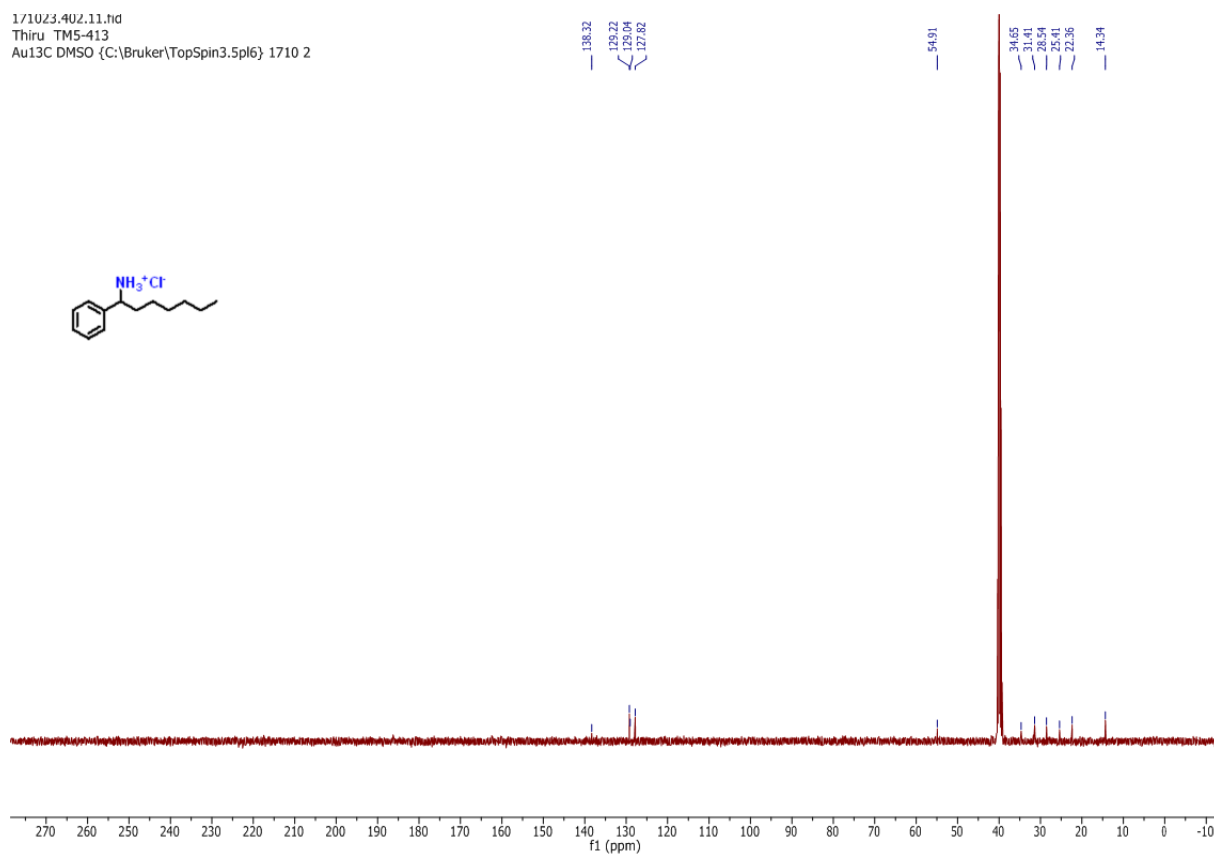
Supplementary Figure 104. ¹³C NMR spectrum

171023.402.10.nd
Thiru TMS-413
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1710 2



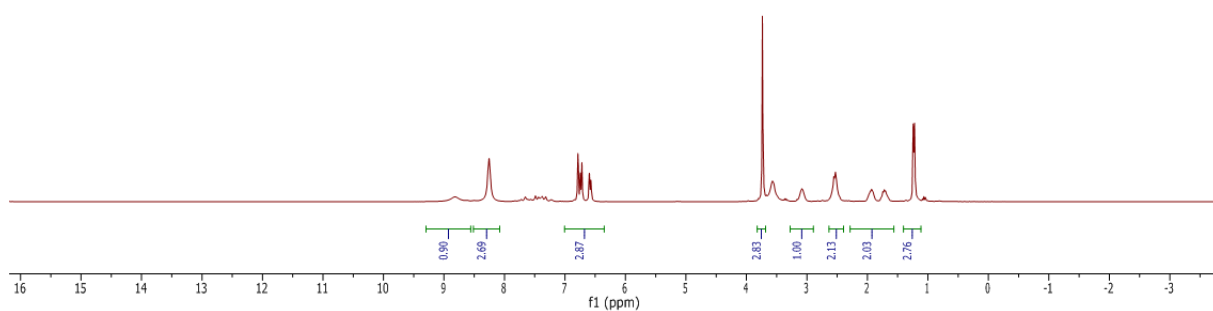
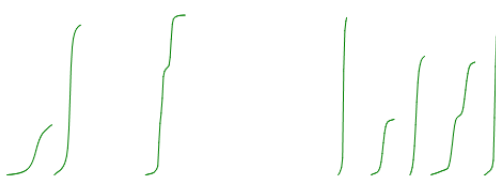
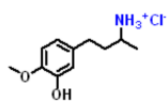
Supplementary Figure 105. ¹H NMR spectrum

171023.402.11.nd
Thiru TMS-413
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1710 2



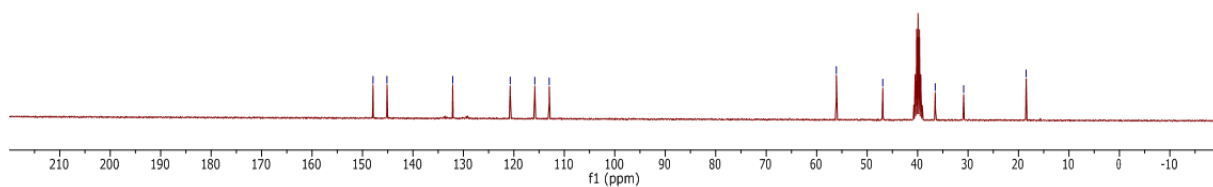
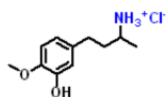
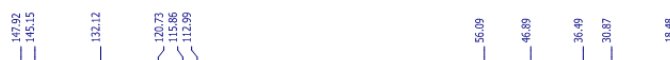
Supplementary Figure 106. ¹³C NMR spectrum

170927.f336.10.fid
Thiru TM5-342
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 36



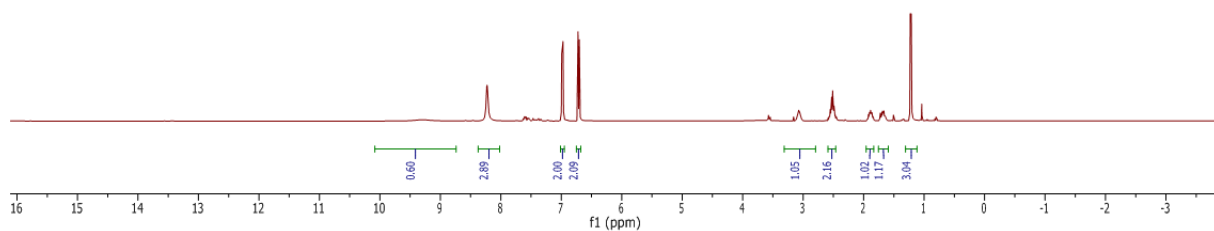
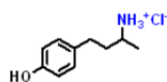
Supplementary Figure 107. ¹H NMR spectrum

170927.f336.11.fid
Thiru TM5-342
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 36



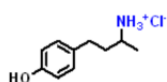
Supplementary Figure 108. ¹³C NMR spectrum

170928.440.10.nd
Thiru TMS-298
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 40



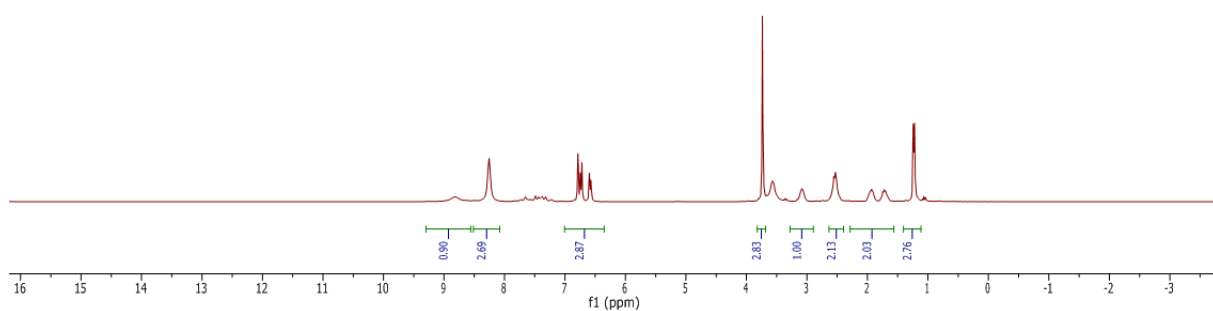
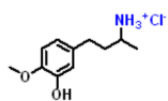
Supplementary Figure 109. ¹H NMR spectrum

170928.440.11.nd
Thiru TMS-298
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 40



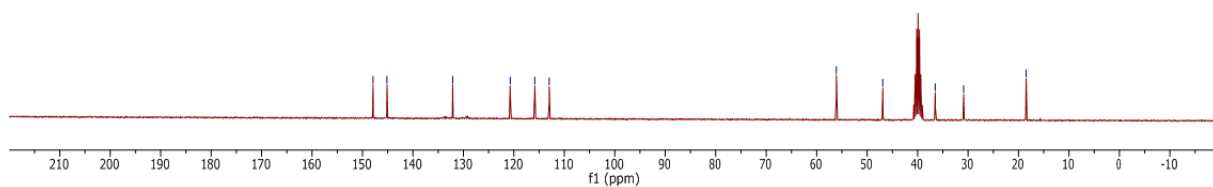
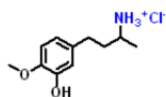
Supplementary Figure 110. ¹³C NMR spectrum

170927.f336.10.fid
Thiru TM5-342
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 36



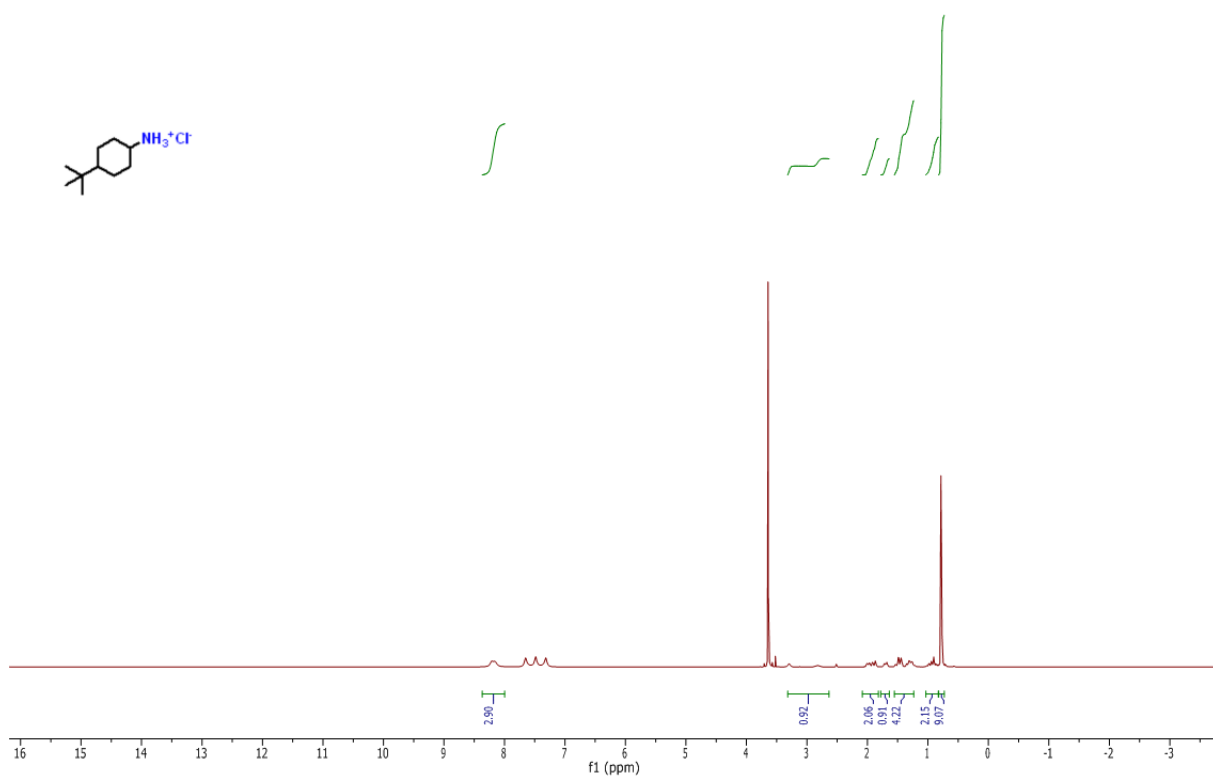
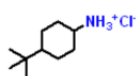
Supplementary Figure 111. ¹H NMR spectrum

170927.f336.11.fid
Thiru TM5-342
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 36



Supplementary Figure 112. ¹³C NMR spectrum

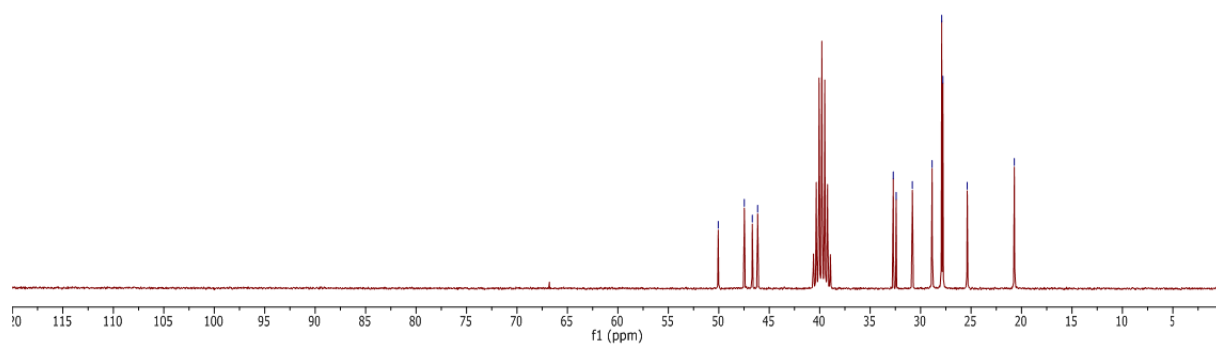
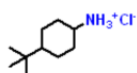
1/0915.f355.10.fid
Thiru TM5-274
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 55



Supplementary Figure 113. ¹H NMR spectrum

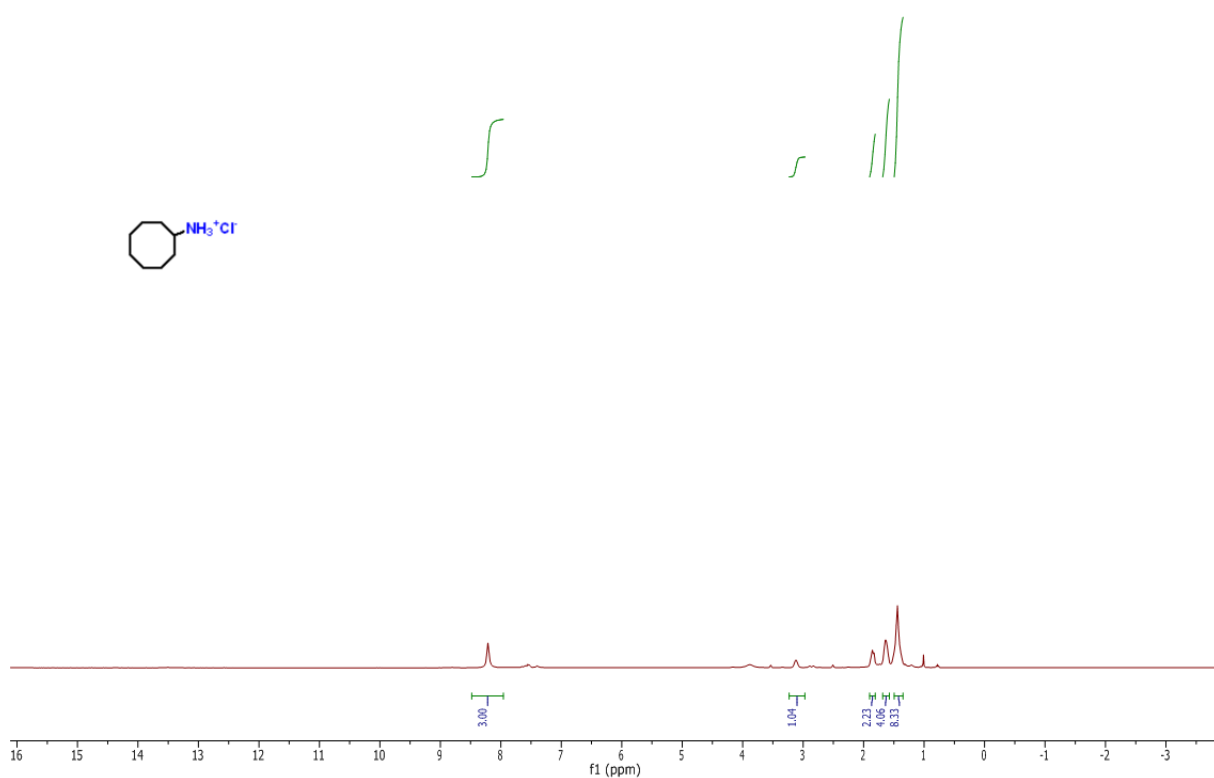
1/0915.f355.11.fid
Thiru TM5-274
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 55

50.05
47.47
46.68
46.15
32.71
32.42
30.81
29.65
27.91
27.79
25.38
20.71



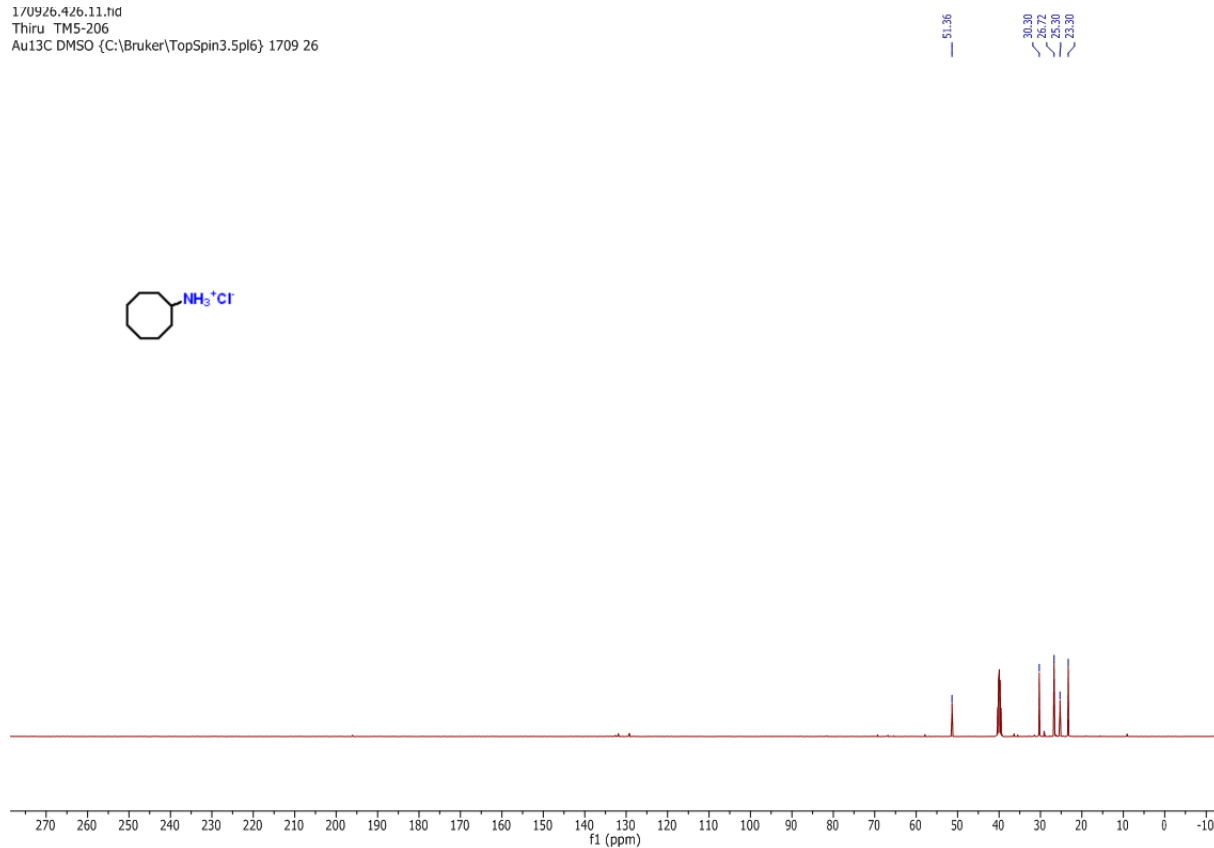
Supplementary Figure 114. ¹³C NMR spectrum

170926.426.10.nd
Thiru TMS-206
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 26



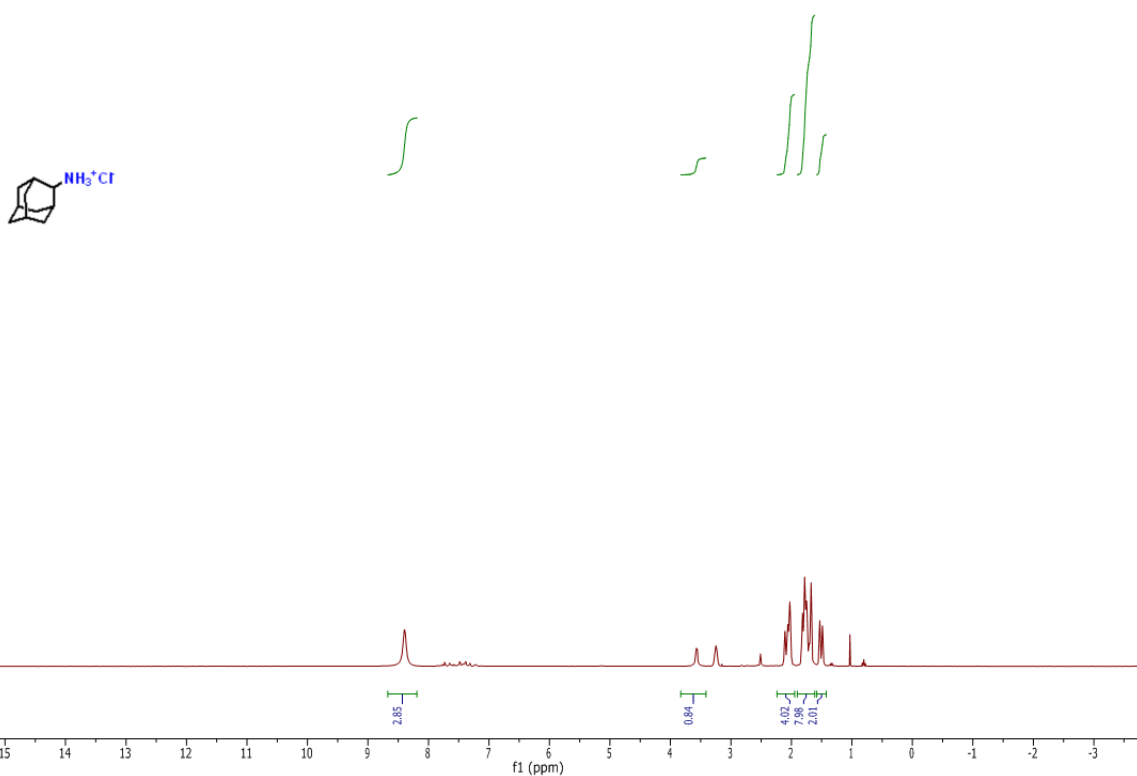
Supplementary Figure 115. ¹H NMR spectrum

170926.426.11.nd
Thiru TMS-206
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 26



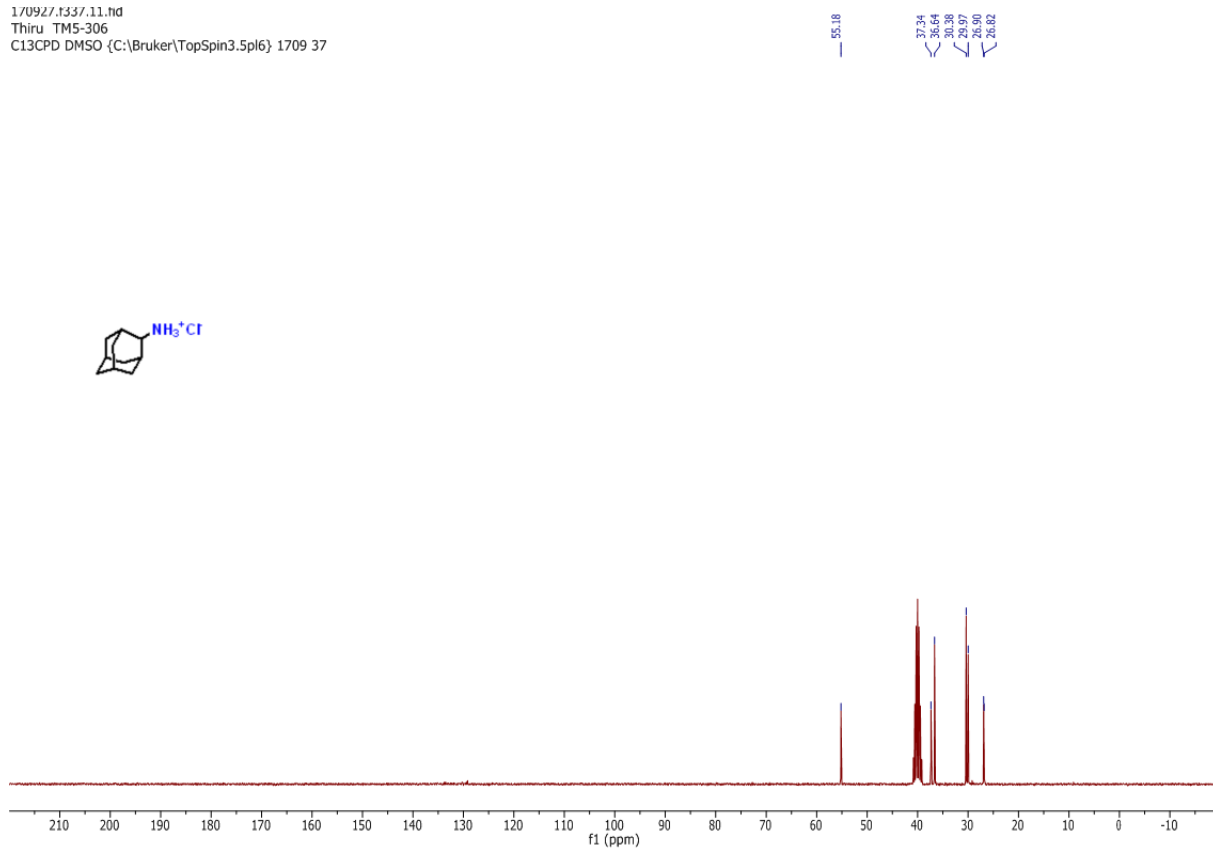
Supplementary Figure 116. ¹³C NMR spectrum

170927.1337.10.nd
Thiru TM5-306
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 37



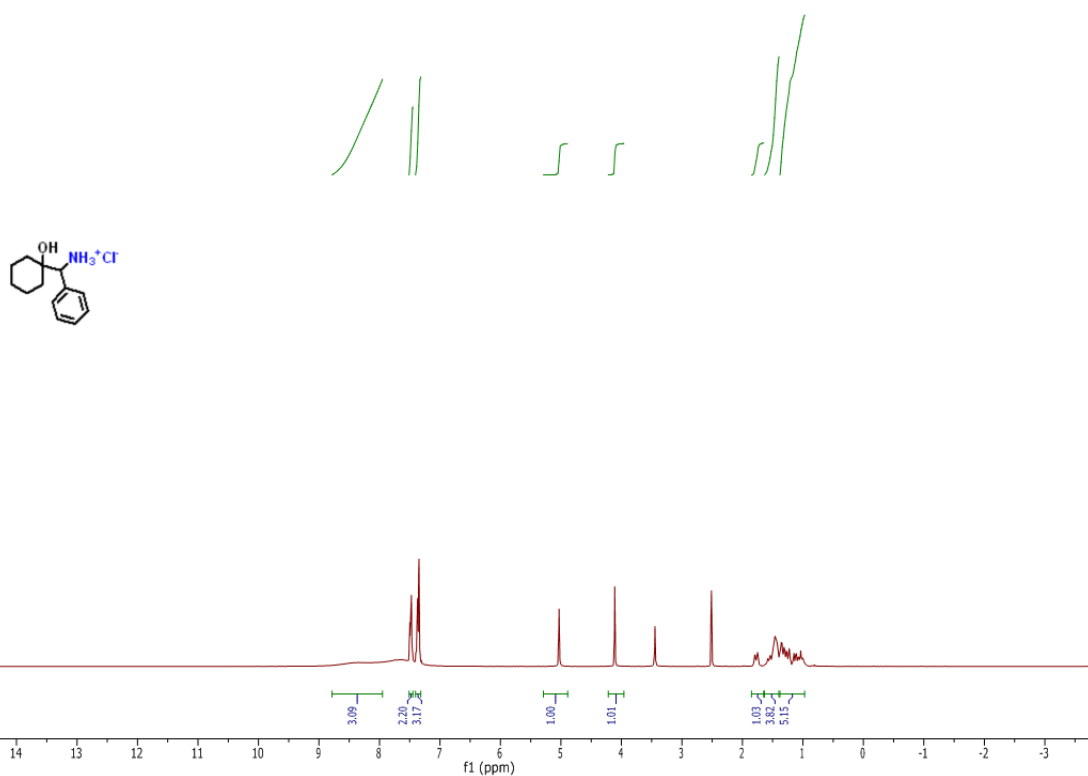
Supplementary Figure 117. ^1H NMR spectrum

170927.1337.11.nd
Thiru TM5-306
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 37



Supplementary Figure 118. ^{13}C NMR spectrum

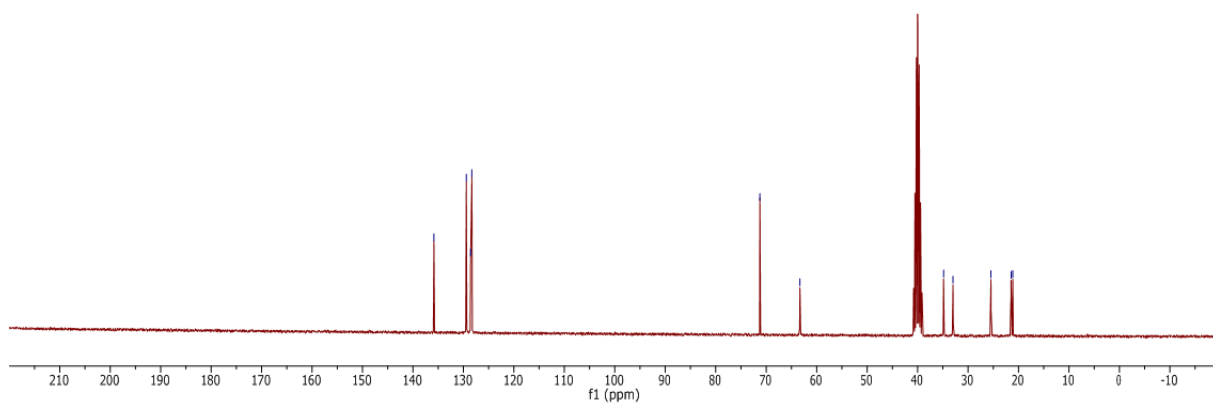
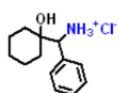
170915.f339.10.fid
Kathir TMS-282
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1709 39



Supplementary Figure 119. ¹H NMR spectrum

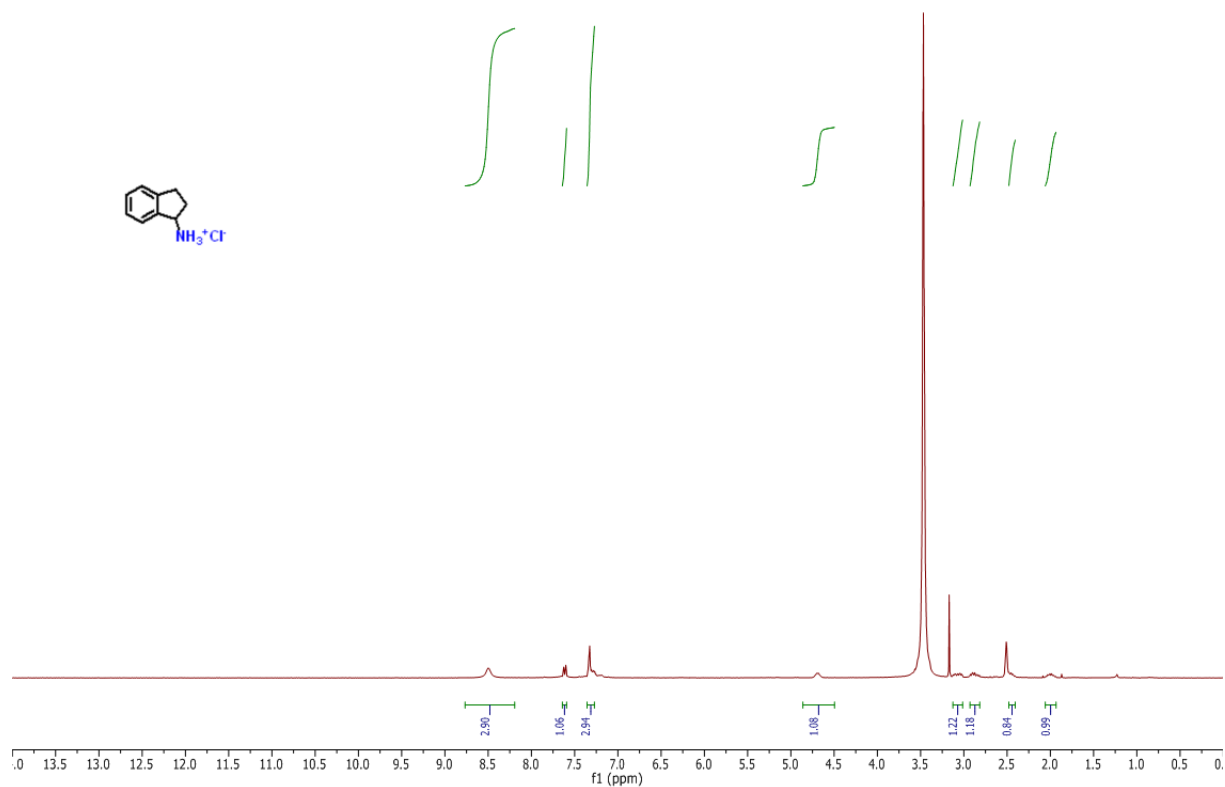
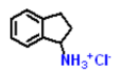
170915.f339.11.fid
Kathir TMS-282
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1709 39

135.84 129.42 128.98 128.33 71.25 63.31 34.85 32.98 25.47 21.47 21.12



Supplementary Figure 120. ¹³C NMR spectrum

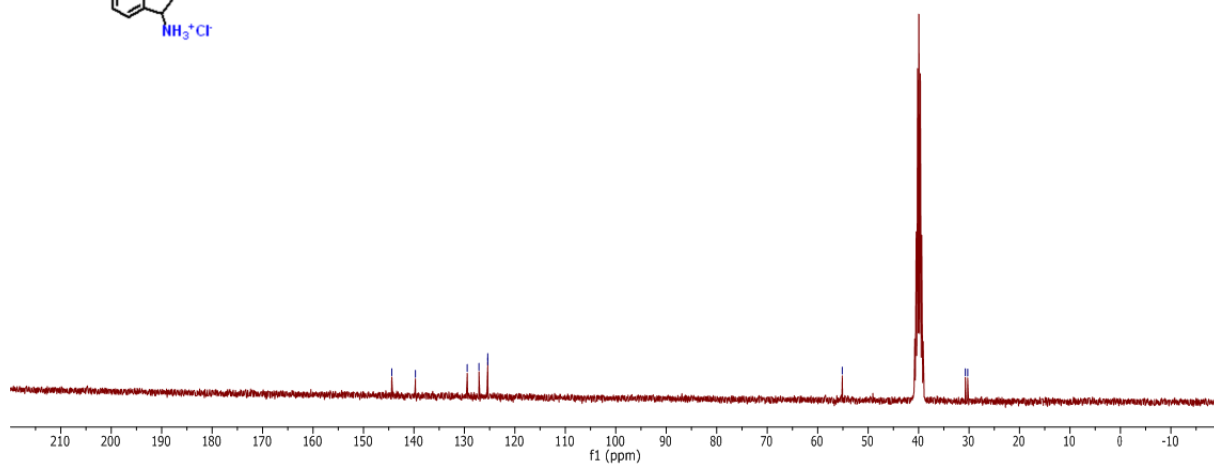
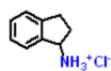
1/1004.f324.10.fid
Thiru TM5-287
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 24



Supplementary Figure 121. ¹H NMR spectrum

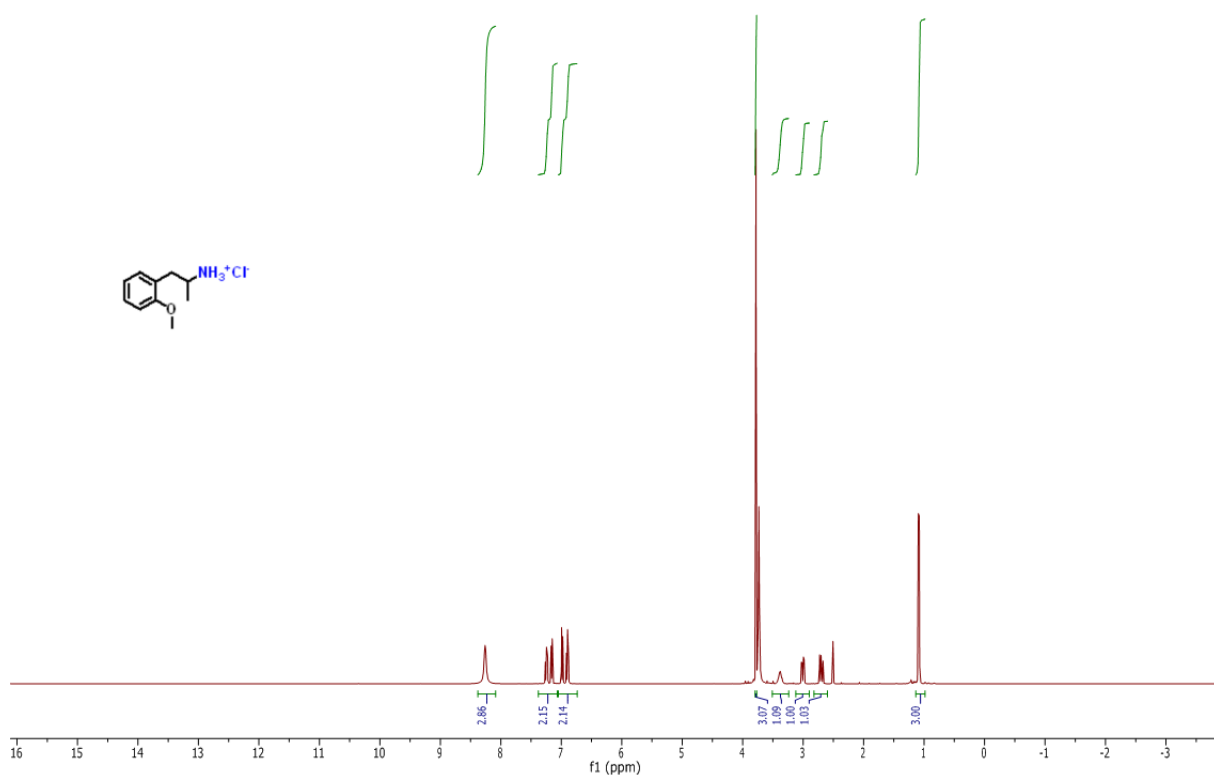
1/1004.f324.11.fid
Thiru TM5-287
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 24

144.39 138.71 128.44 127.11 126.38 125.37 55.12 30.73 30.27



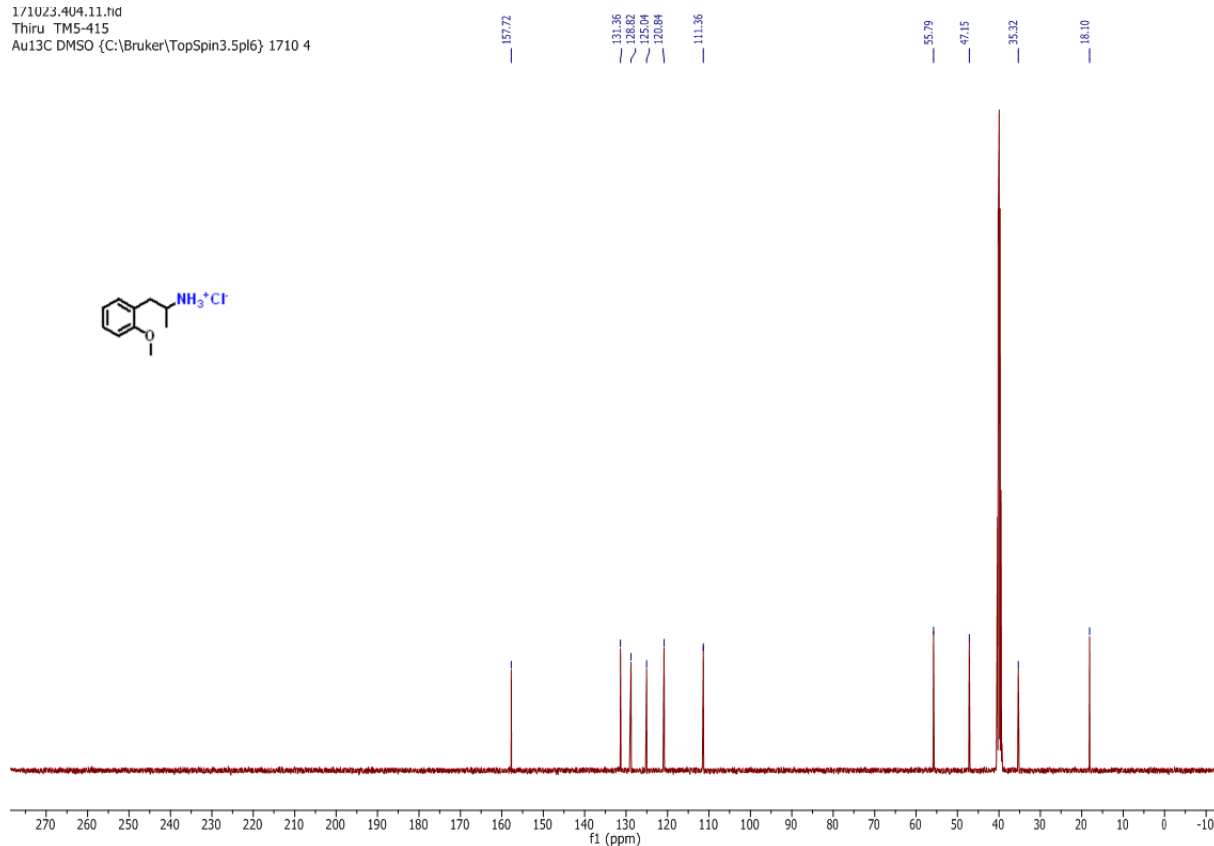
Supplementary Figure 122. ¹³C NMR spectrum

1/1023.404.10.nd
Thiru TMS-415
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1710 4



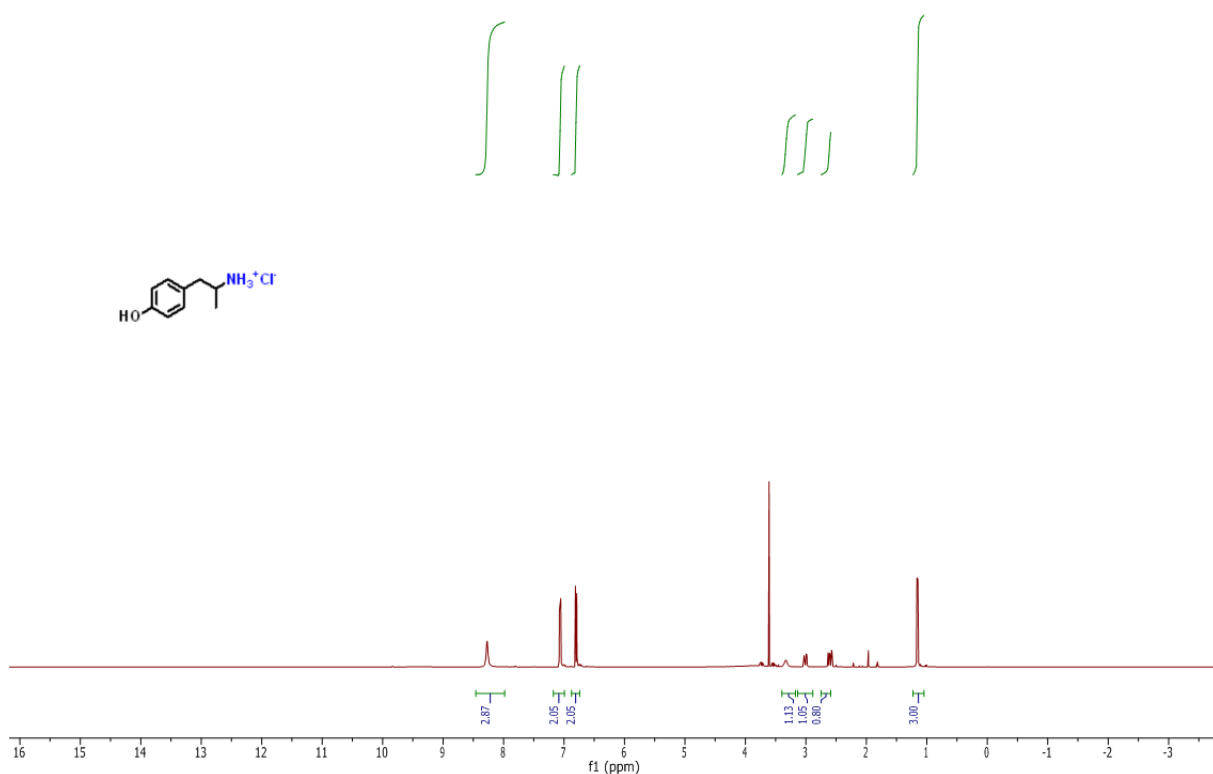
Supplementary Figure 125. ¹H NMR spectrum

1/1023.404.11.nd
Thiru TMS-415
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1710 4



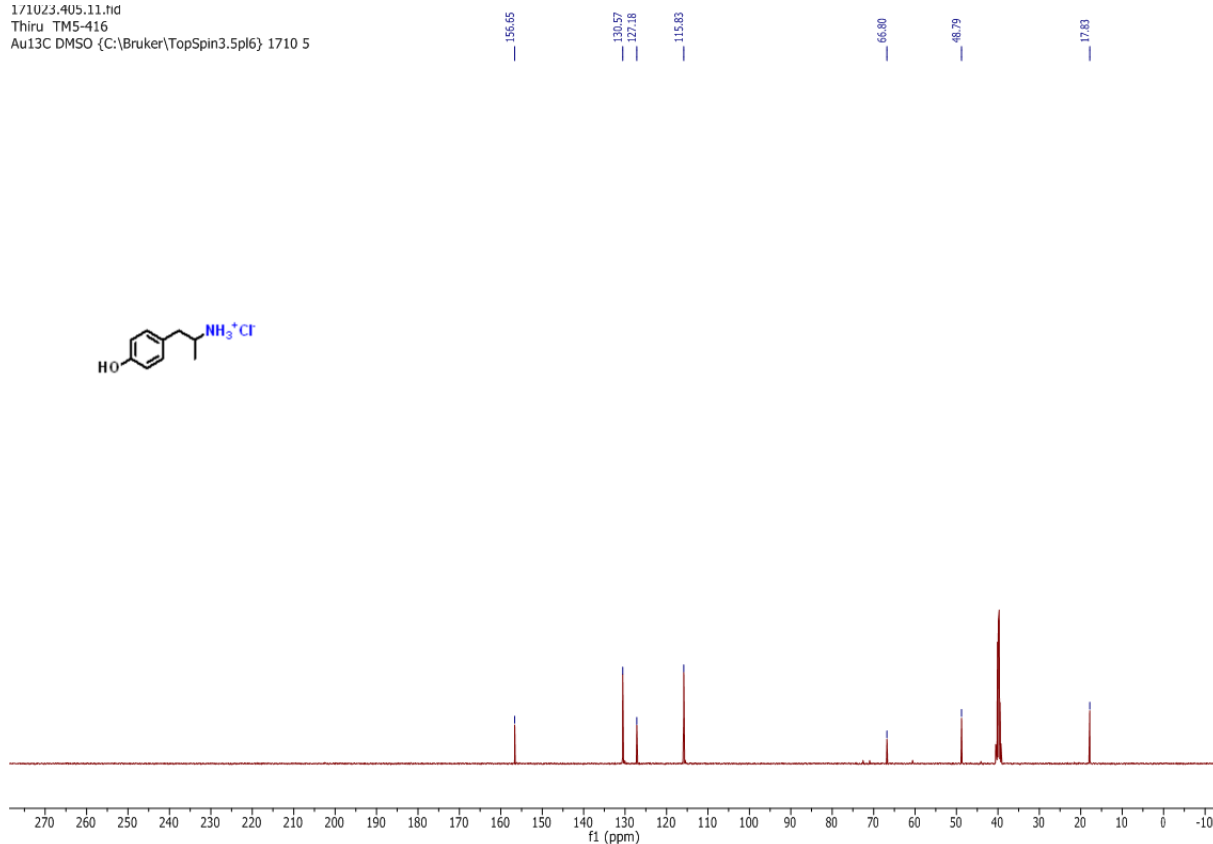
Supplementary Figure 126. ¹³C NMR spectrum

171023.405.10.nd
Thiru TMS-416
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1710 5



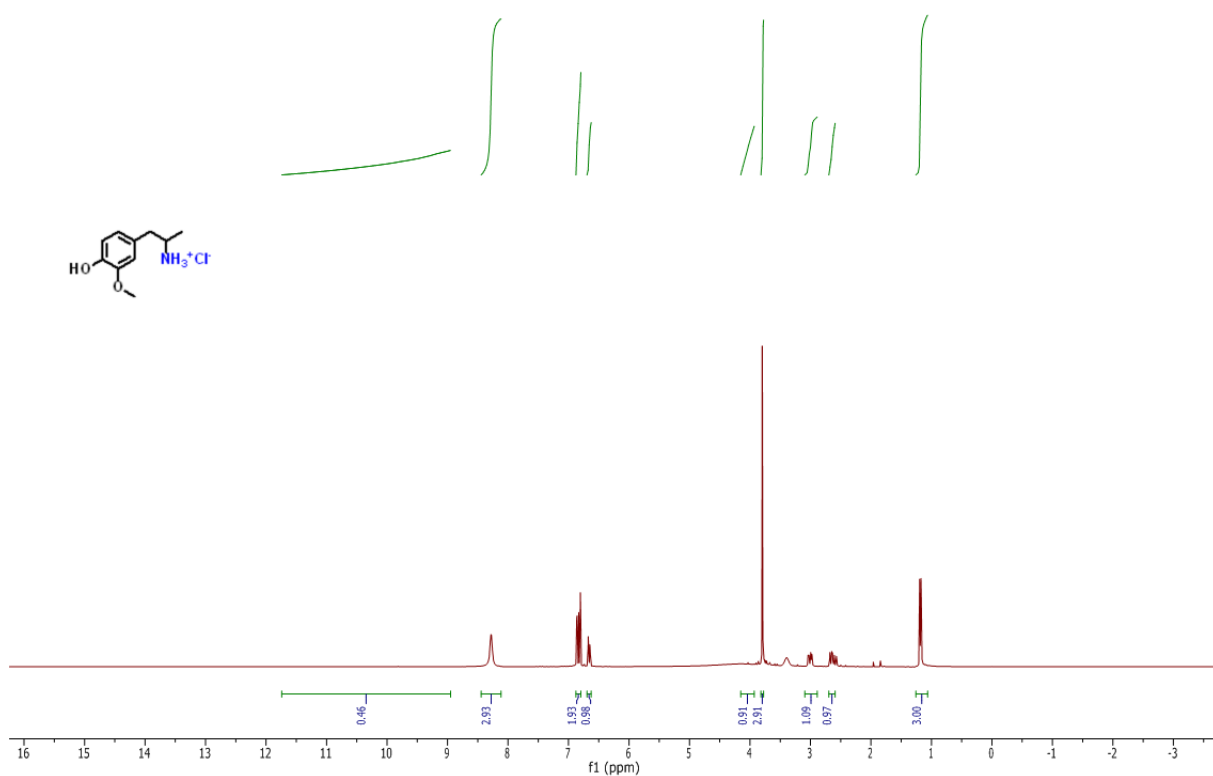
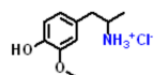
Supplementary Figure 127. ¹H NMR spectrum

171023.405.11.nd
Thiru TMS-416
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1710 5



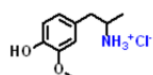
Supplementary Figure 128. ¹³C NMR spectrum

1/1004.f315.10.fid
Thiru TMS-207
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 15



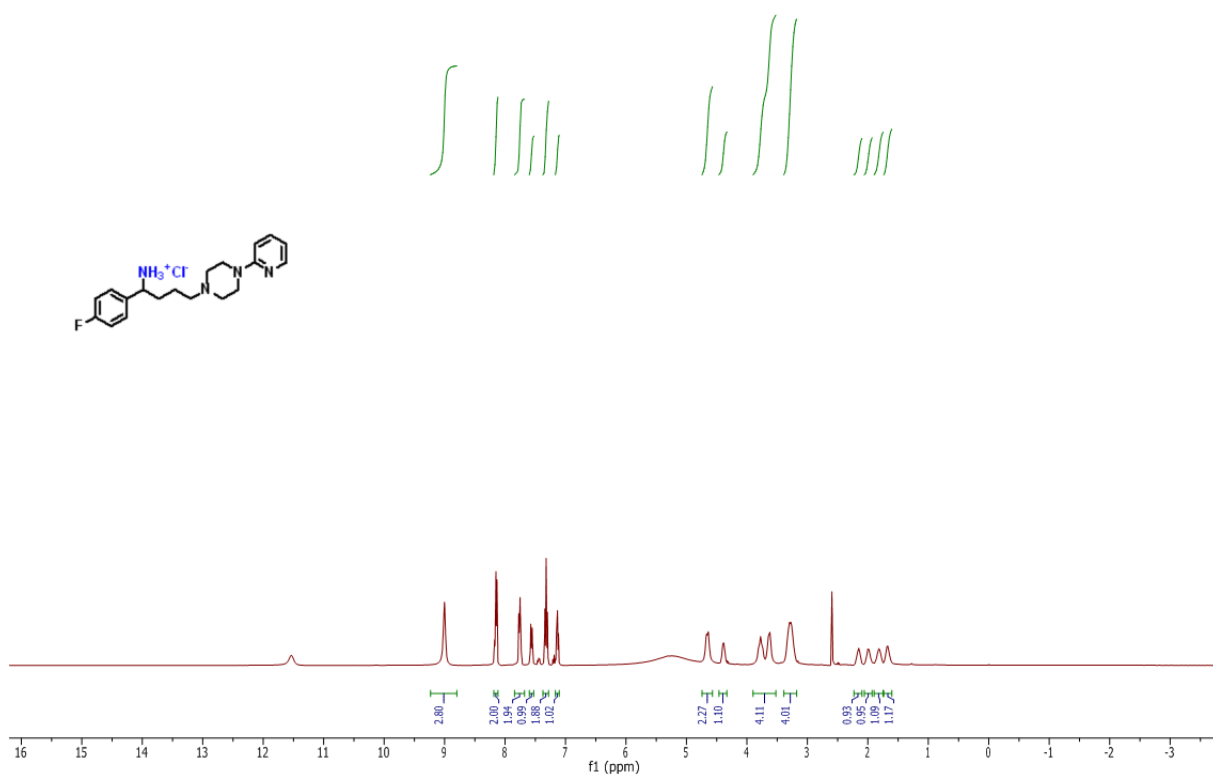
Supplementary Figure 129. ¹H NMR spectrum

1/1004.f315.11.fid
Thiru TMS-207
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 15



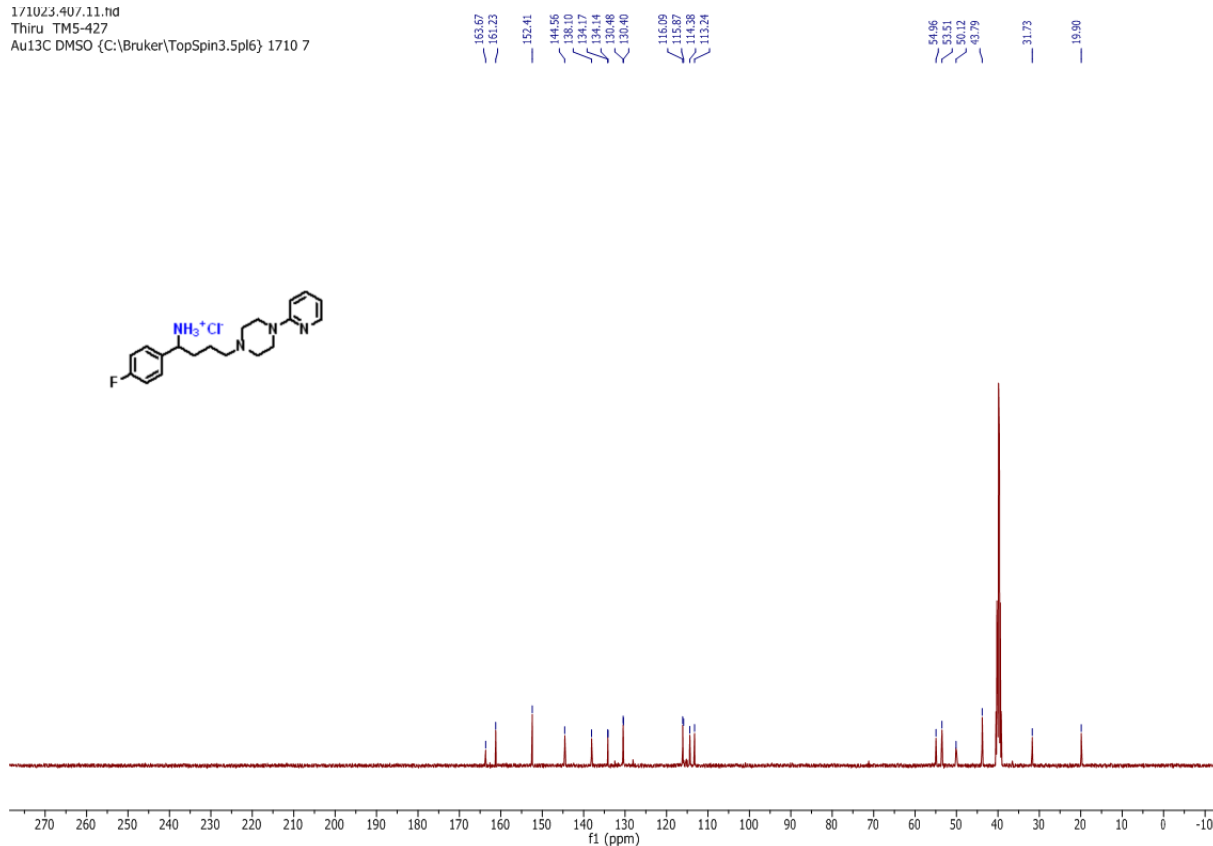
Supplementary Figure 130. ¹³C NMR spectrum

1/1023.407.10.nd
Thiru TM5-427
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1710 7



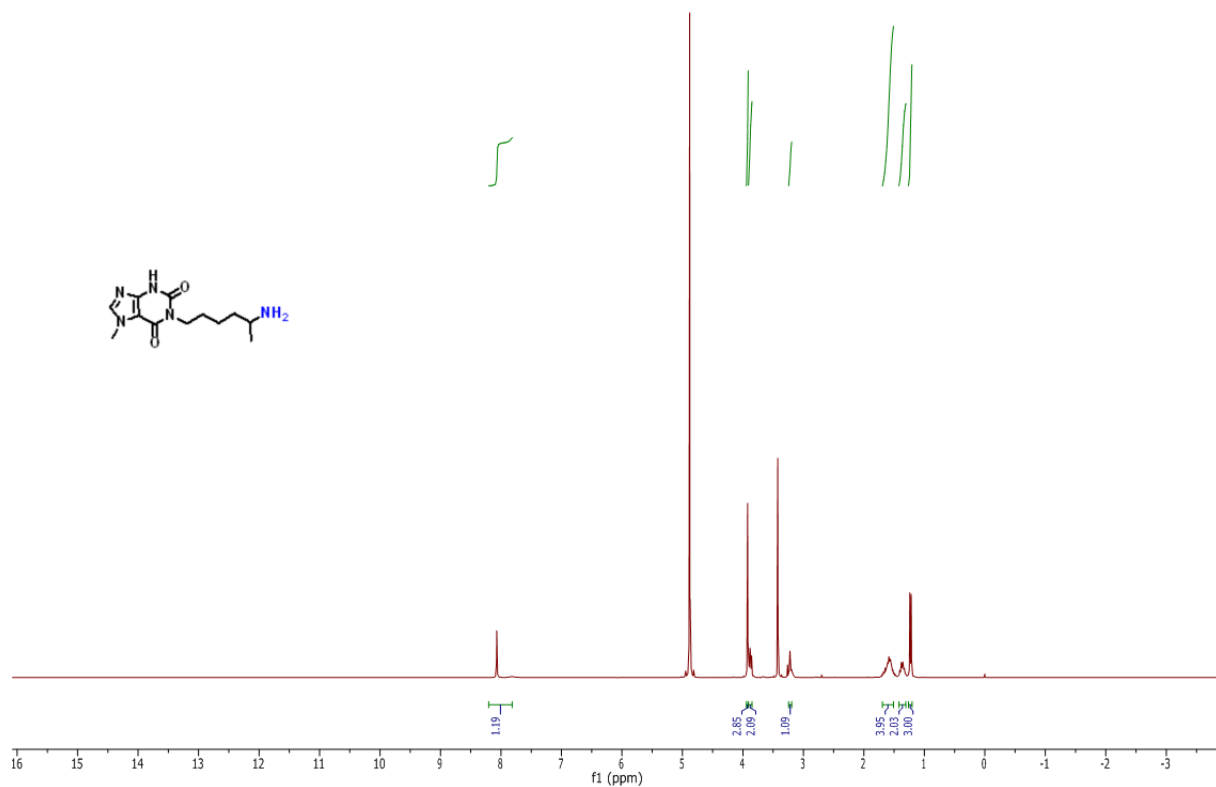
Supplementary Figure 131. ¹H NMR spectrum

1/1023.407.11.nd
Thiru TM5-427
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1710 7



Supplementary Figure 132. ¹³C NMR spectrum

171030.f328.10.fid
Thiru TM5-428
PROTON MeOD {C:\Bruker\TopSpin3.5pl6} 1710 28



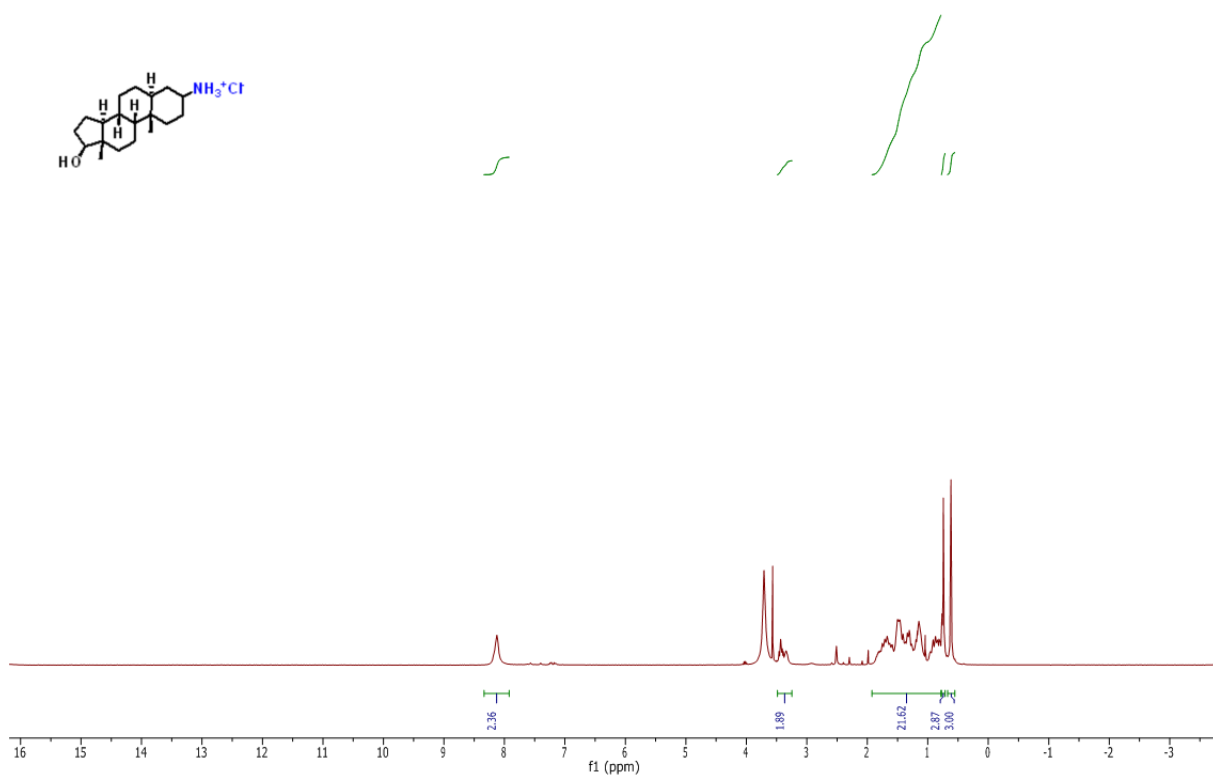
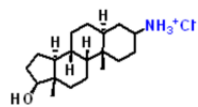
Supplementary Figure 133. ^1H NMR spectrum

171030.f328.11.fid
Thiru TM5-428
C13CPD MeOD {C:\Bruker\TopSpin3.5pl6} 1710 28



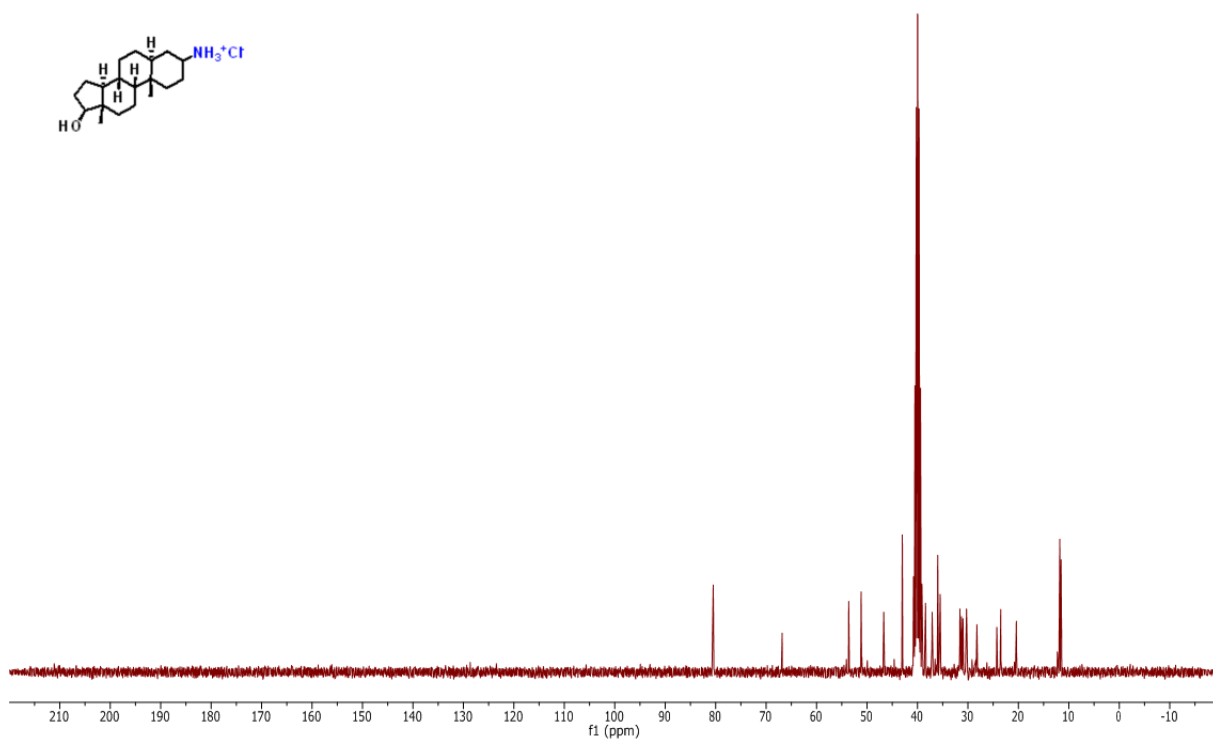
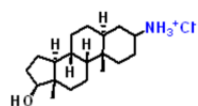
Supplementary Figure 134. ^{13}C NMR spectrum

1/1221.f330.10.fid
Thiru, TM5-307
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1712 30



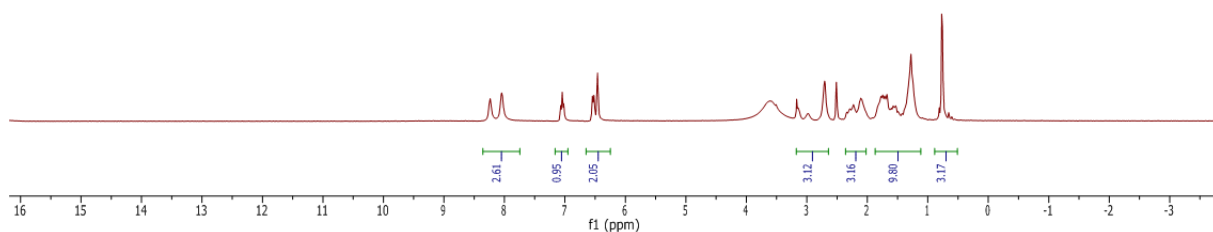
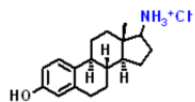
Supplementary Figure 135. ¹H NMR spectrum

1/1221.f330.11.fid
Thiru, TM5-307
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1712 30



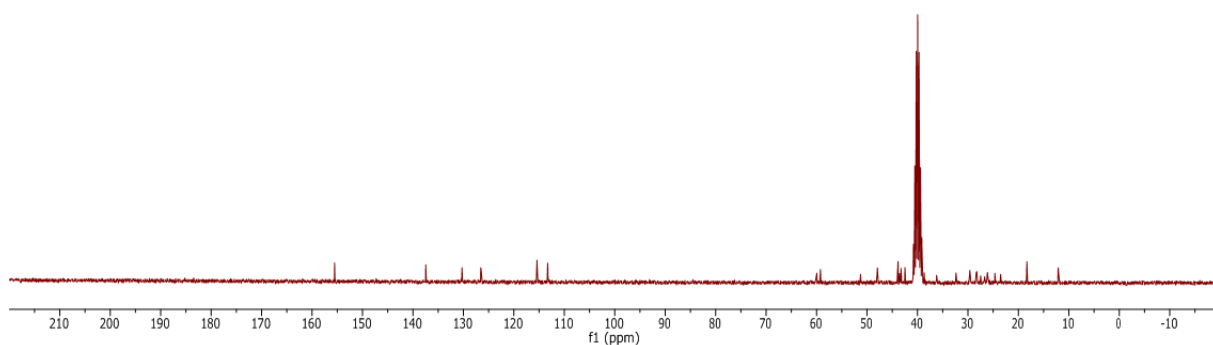
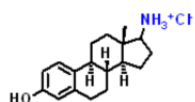
Supplementary Figure 136. ¹³C NMR spectrum

1/1006.f325.10.fid
Thiru TMS-363
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1710 25

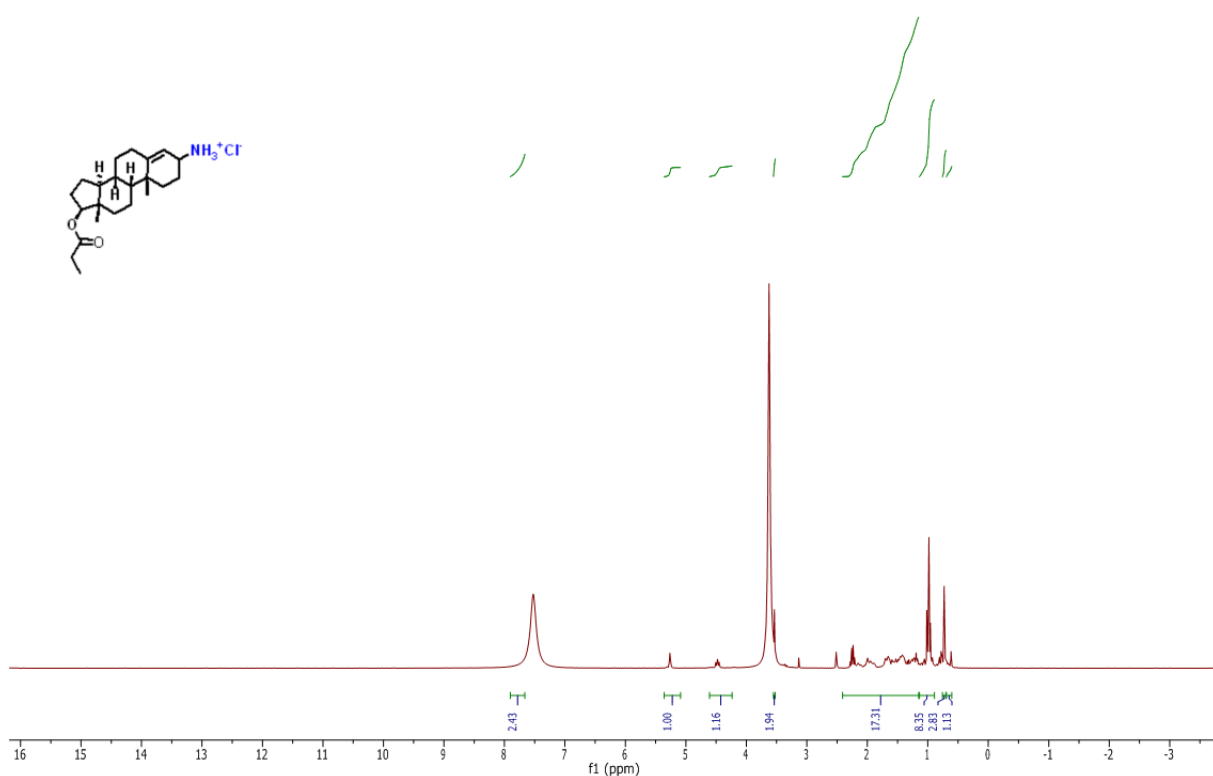


Supplementary Figure 137. ¹H NMR spectrum

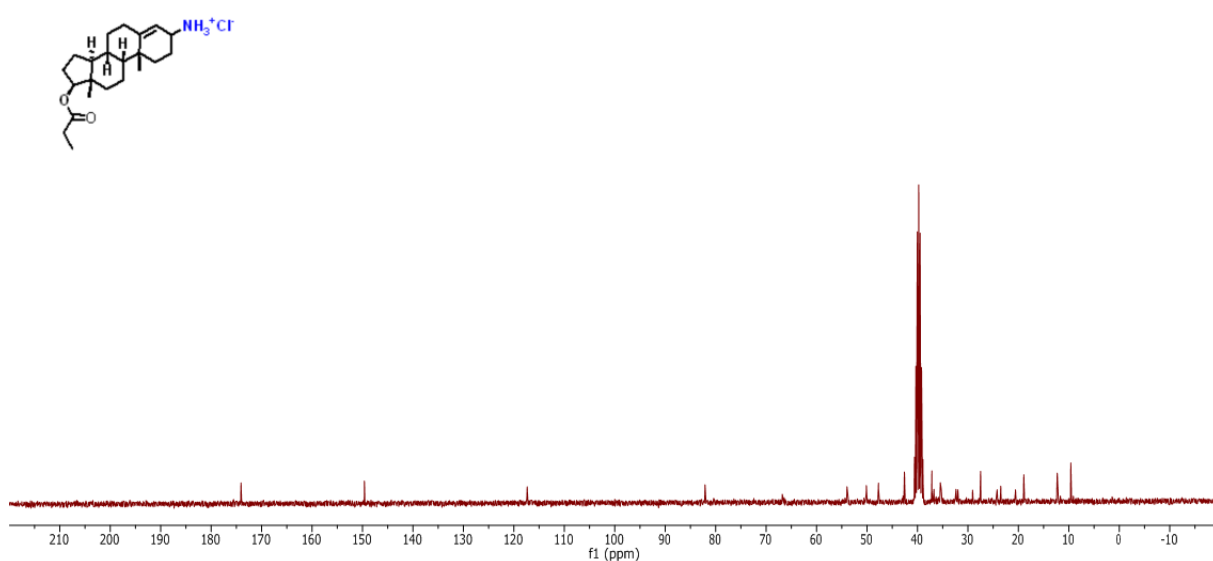
1/1006.f325.11.fid
Thiru TMS-363
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1710 25



Supplementary Figure 138. ¹³C NMR spectrum

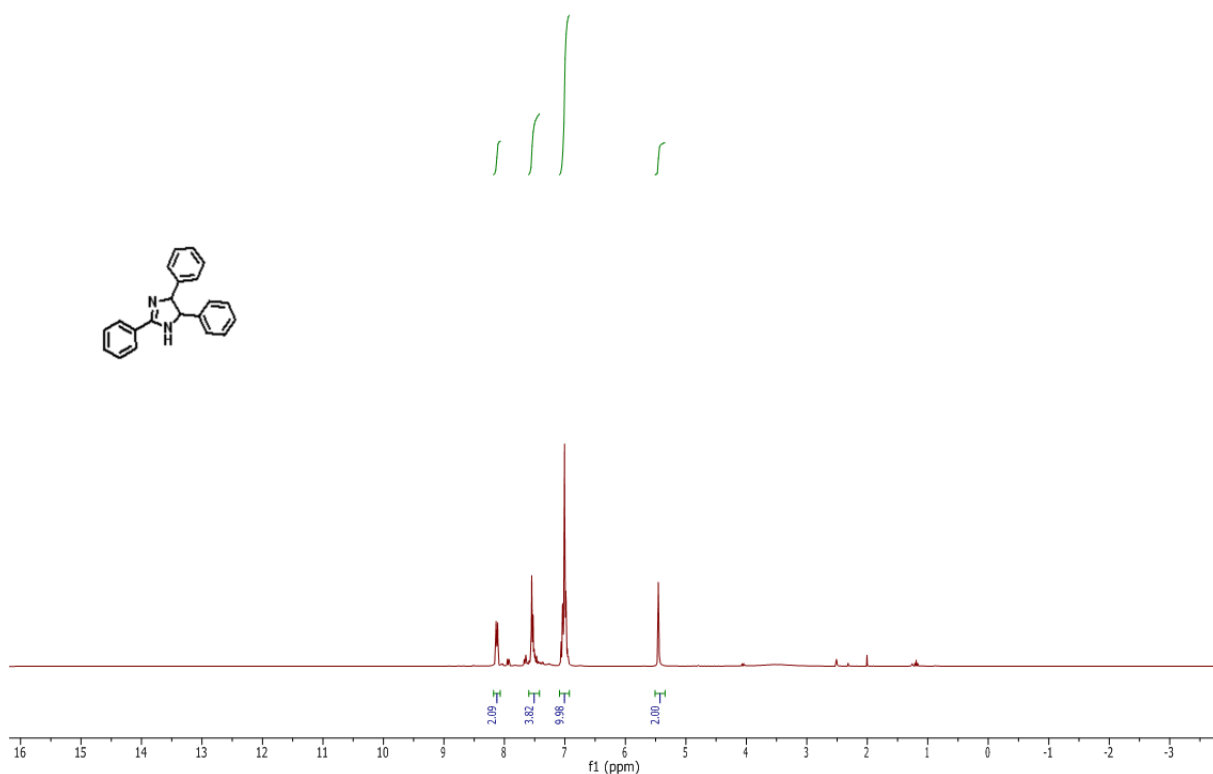


Supplementary Figure 139. ¹H NMR spectrum



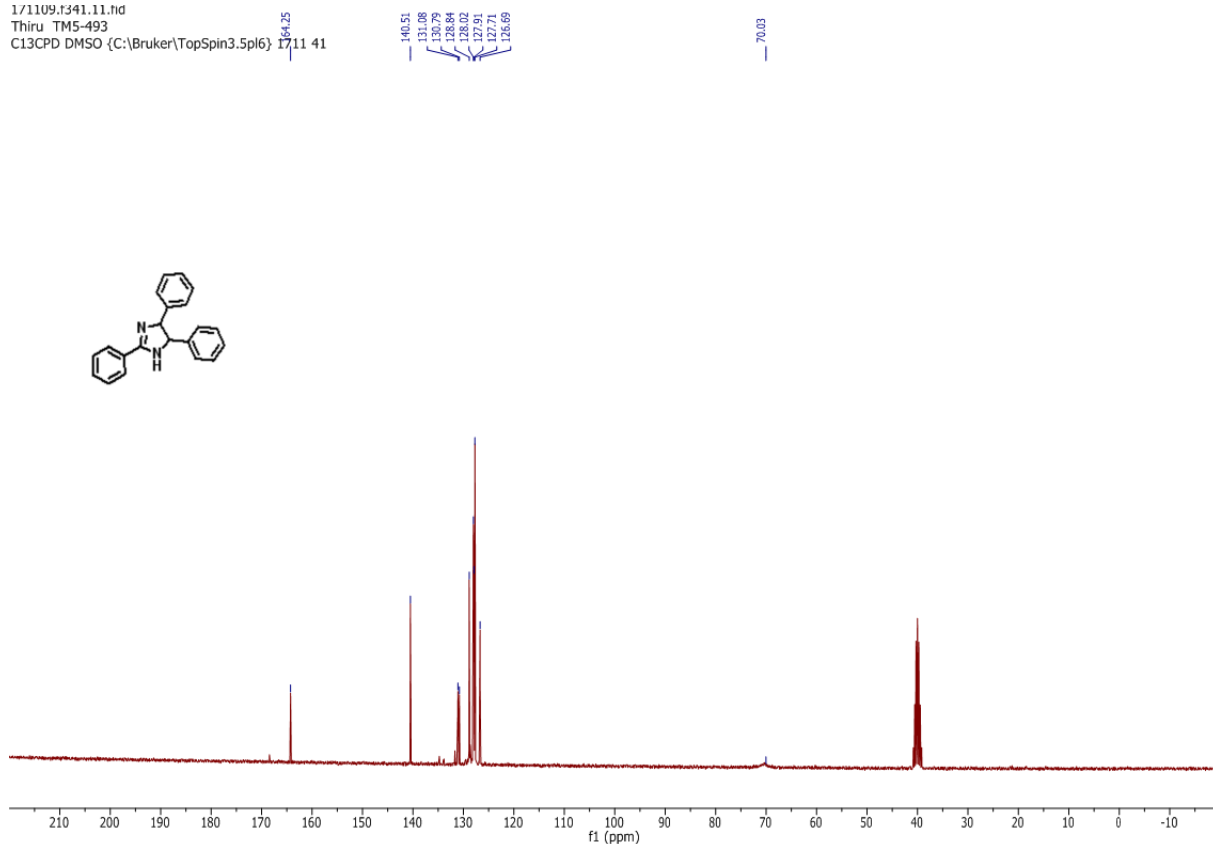
Supplementary Figure 140. ¹³C NMR spectrum

1/1109.f341.10.fid
Thiru TMS-493
PROTON DMSO {C:\Bruker\TopSpin3.5pl6} 1711 41



Supplementary Figure 141. ¹H NMR spectrum

1/1109.f341.11.fid
Thiru TMS-493
C13CPD DMSO {C:\Bruker\TopSpin3.5pl6} 1711 41



Supplementary Figure 142. ¹³C NMR spectrum